NANOYOU Teachers Training Kit in Nanoscience and Nanotechnologies
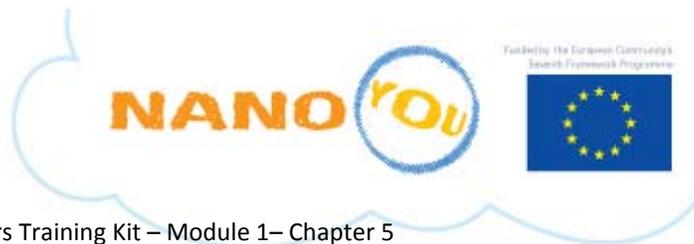
Chapter 5 – Overview of Nanomaterials

Module 1- Fundamental concepts in nanoscience and nanotechnologies

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Chapter 5: Overview of Nanomaterials

This chapter provides an overview of nanomaterials, their properties and functions. The application areas of the cited nanomaterials are also mentioned. The second Module of this Teachers Training Kit is devoted to applications of nanotechnologies.

Biomimetic nanomaterials

The first class of engineered nanomaterials that we review is Biomimetic materials. As mentioned in **Chapter 2 of Module 1 ("Natural Nanomaterials")**, **Nature is the best nanotechnology platform**. Through thousands of years of evolution Nature has developed an enormous array of materials, ranging from feathers, to shells, wood, bone and many more that have intricate hierarchical structures at the nano, micron and macro levels which confer specific properties on the material, such as strength, lightweight, permeability, colour, etc. Natural materials provide an amazing platform inspiring material engineers to fabricate advanced materials that possess specific functions. As a matter of fact numerous "macro" materials we use today were developed after inspiration from natural materials. One example is Velcro, which was developed in 1948 by a Swiss engineer named George de Mistral who was inspired by the mechanism that enables *cockleburs* to cling to dog hair and fabric. Nanostructures in the natural material often play a crucial role, which inspires scientists to mimic them starting from a molecular level (molecular biomimetics). This is also called biomimetic nanotechnology. Here we provide some examples of these biomimetic nanomaterials.

Gecko-inspired adhesive (or Bio-rubber)

In **Chapter 2** we discussed the adhesive properties of the gecko foot, and how these are not related to a glue in the foot, but rather to van der Waals and capillary forces exerted by millions of nanostructures (called setae) that make up the foot. This allows the animal to walk upside down, against gravity, on many different surfaces, even on wet ones. Moreover a gecko can walk on a dirty surface without losing adherence, since its feet are also self-cleaning. A truly amazing material! Scientists have been inspired by this animal to design and fabricate adhesives for numerous applications. For instance a group of researchers at the University of California, Berkeley, has developed adhesive gecko-foot-like surfaces for use in climbing robots. The adhesive is made of patches of microfiber arrays with 42 million polypropylene microfibers per cm^2. The patches can support up to 9 N cm^{-2}: a 2 cm^2 patch can support a load of 400 g. This result is very close to the loads supported by a gecko, which are about 10 N cm^{-2}. This

gecko-like adhesive is very similar in functionality to the natural gecko foot, but yet not as good. Researchers still have to make it topography-independent (capable of attaching to any surface) and self-cleaning. In another university a biomimetic gecko tape has been produced using polymer surfaces covered with carbon nanotube hairs, which can stick and un-stick on a variety of surfaces, including Teflon.

Other gecko-inspired nanomaterials are under development for medical applications, which will be covered in **Chapter 1 of Module 2 ("Applications of Nanotechnologies: Medicine & Healthcare")**.

Self-healing adhesives

Diatoms are a type of algae with nanostructured amorphous silica surfaces. Some diatom species have evolved strong self-healing underwater adhesives. Some are free-floating; others have adhesive properties in water: for instance diatoms in the Antarctic seas can attach to ice. Others secrete viscous mucilage which binds colonies together while protecting the silica shells from wear as they rub against each other. Molluscs are another species of animals that have **adhesive properties under water**. Both diatoms and molluscs have strong underwater glues that can also resist stress and self-heal if necessary. For these reasons they serve as a biomimetic model for self-healing materials. Researchers have studied these natural adhesives and found that their self-healing properties are due to the properties of the proteins that compose them. These proteins have "sacrificial" bonds that allow the molecule to be reversibly stretched by their breaking and re-bonding. This sacrificial bond behaviour has been observed in many other materials, such as wool. The detailed analysis of these natural materials is inspiring new nano-adhesives with self-healing properties.

Biomimetic membranes, capsules and bioreactors

The bilipid membrane has served as a biomimetic model for decades. A simple example is liposomes (lipid vesicles) which are easily formed by shaking oil vigorously in water. Planar supported bilayers are also inspired by the lipid membrane and are formed by simply "dipping" a suitable substrate inside an organic aqueous phase.

Inside the cell there are numerous self-assembled structures that encapsulate specific biomolecules and release them as a consequence of molecular signalling. These structures are inspiring a wide range of **nanocapsules for application in drug delivery**. In some cases bacteria or viruses are used as templates for fabricating these nanocapsules. These

nanomaterials are described in more detail in **Chapter 1 of Module 2 ("Applications of Nanotechnologies: Medicine & Healthcare")**.

Biomimetic energy nanomaterials

Many challenges that we are now facing in the energy area (improvements needed in solar panels, hydrogen fuel cells, rechargeable batteries etc.) can be solved through the use of nano-engineered materials. Some of these materials are developed through direct inspiration from Nature, such as the new types of solar photovoltaic cells, which try to imitate the natural nanomachinery of photosynthesis. Another interesting example is that of using battery electrodes with self-assembling nanostructures grown by genetic engineered viruses.

Both examples will be described in more detail in **Chapter 3 of Module 2 ("Applications of Nanotechnologies: Energy")**

NANOYOU GAME Nature-inspired nanomaterials are used in one of the NANOYOU Jigsaw puzzle game. Students need to match the nanomaterial, to its application, connecting it to a specific need. The game can be found at:

http://nanoyou.eu/en/play-nano.html

Self-assembled nanomaterials

The concept of self-assembly derives from observing that, in natural biological processes, molecules self-assemble to create complex structures with nanoscale precision. Examples are the formation of the DNA double helix or the formation of the membrane cell from phospholipids. In self-assembly, *sub-units spontaneously organise and aggregate into stable, well defined structures through non covalent interaction*. This process is guided by information that is coded into the characteristics of the sub-units and the final structure is reached by equilibrating to the form of the lowest free energy. An external factor, such as a change in temperature or a change in pH, can disrupt this organisation. For instance, a protein self-assembles in a specific structure, but if exposed to conditions such as high heat or high acidity, it can denature, which means that its structure is damaged, and the protein unfolds. This means that the protein loses its function as its structure is damaged. So in Nature self-organised structures have specific functions.

Molecules in Nature change conformation and move from one self-organised structure into another as they bind to certain ions or atoms. Many examples could be given, like haemoglobulin (which captures and releases an iron ion), or the potassium-sodium pump, chlorophyll, etc.

The use of self-assembly to create new materials is a bottom-up approach to nanofabrication, and is thus an essential tool in nanotechnology (see **Chapter 7 of Module 1 "Fabrication techniques"**). Instead of carving nanostructures out of larger materials (which is the typical top-down approach, like micromachining and microlithography, used to fabricate integrated electronic circuits), nanostructures are created from the bottom, from atomic building blocks that self-assemble in larger structures. In the laboratory scientists can make use of this self-organisation of matter as a way of programming the building of novel structures with specific functions.

Liquid crystals

A liquid crystal is a fourth state of matter: it has properties between those of a conventional liquid and those of a solid crystal. Like a liquid, it flows, and like a crystal, it can display long-range molecular order (**Figure 1**). In terms of classifications, LCs (together with polymers and colloids), are often classified as "soft matter" (**Figure 2**) and treated under the branch of physical chemistry of condensed matter.
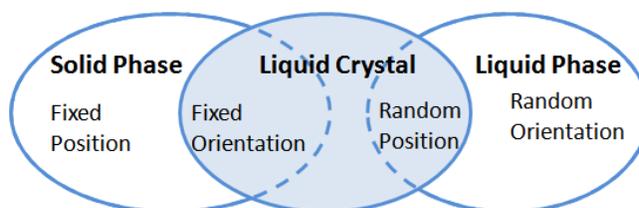
Figure 1. The liquid crystal phase is in between a solid and a liquid phase (Image credit: L. Filipponi, iNANO, Aarhus University, Creative Commons Attribution ShareAlike 3.0).
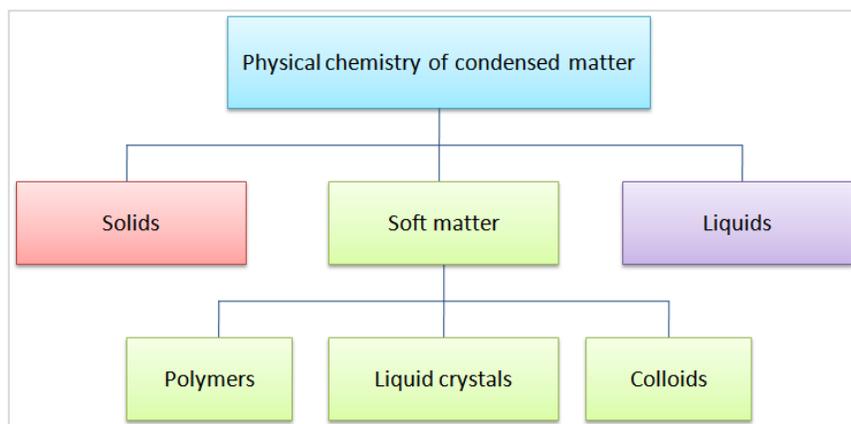
Figure 2. Diagram showing where the branch of "liquid crystals" fits into the classification of physical chemistry of condensed matter.

A fascinating and characteristic feature of liquid-crystalline systems is that they change their molecular and supermolecular organisation drastically as an effect of very small external perturbations: The molecules in liquid crystal displays for instance are reoriented by relatively weak electrical fields. If one dissolves a small amount of chiral molecules in an achiral liquid-crystalline host phase, this results in remarkable macroscopic chirality effects, ranging from helical superstructures to the appearance of ferroelectricity.

Liquid crystal self-assembly

Liquid crystals are partly ordered materials, somewhere between their solid and liquid phases. This means that LCs combine the fluidity of ordinary liquids with the interesting electrical and optical properties of crystalline solids.

The molecules of liquid crystals are often shaped like rods or plates or some other forms that encourage them to align collectively along a certain direction (**Figure 5**).

Figure 5. Example of the self-organisation of anisometric (i.e., with asymmetrical parts) molecules in liquid-crystalline phases. On the left: rod-like molecules form a nematic liquid, in which the longitudinal axes of the molecules are aligned parallel to a common preferred direction ("director"). On the right: disc-like (discotic) molecules arrange to molecule-stacks (columns), in which the longitudinal axes are also aligned parallel to the director. As a result of their orientational order, liquid crystals exhibit anisotropic physical properties, just like crystals. (Reprinted from: http://www.ipc.uni-stuttgart.de/~giesselm/AG_Giesselmann/Forschung/Fluessigkristalle/Fluessigkristalle.html).

Liquid crystals are **temperature sensitive** since they turn into solid if it is too cold and into liquid if it is too hot. This phenomenon can, for instance, be observed on laptop screens when it is very hot or very cold.

Liquid crystals´ phases and their properties

A liquid crystal is formed by the self-assembly of molecules in ordered structures, or phases. An external perturbation, such as a change in temperature or magnetic field, even very small, can induce the LC to assume a different phase. Different phases can be distinguished by their different optical properties (**Figure 3**).
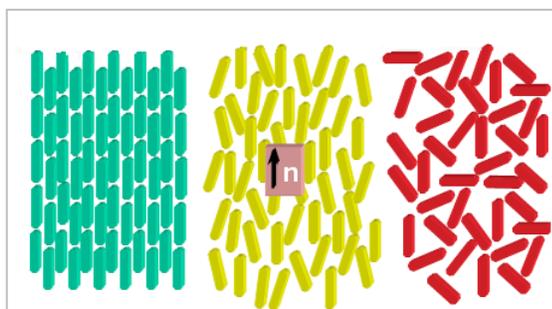
Figure 3. Schematic representation of molecules in a solid (left, molecules are well organised), in a liquid crystal (centre) molecules have a long range distance order) and in a liquid (right) molecules are not ordered. (Image credit: Copyright IPSE Educational Resources, University of Wisconsin Madison)

Liquid crystals are divided into three groups:

- **Thermotropic LC**: they consist of organic molecules, typically having coupled double bonds, and exhibit a phase transition as temperature is changed (**Figure 4, left**);

- **Lyotropic LC**: they consist of organic molecules, typically amphiphilic (water-loving) and exhibit a phase transition as a function of both temperature and concentration of the LC molecules in a solvent (typically water) (**Figure 4, right**);

- **Metallotropic LC**: they are composed of both organic and inorganic molecules, and their LC transition depends not only on temperature and concentration, but also on the organic-inorganic composition ratio.

Figure 4. (**Left**) chemical structure of N-(4-Methoxybenzylidene)-4-butylaniline (MBBA); (Right): Structure of lyotropic liquid crystal: 1 is a bilayer and 2 is a micelle. The red heads of surfactant molecules are in contact with water, whereas the tails are immersed in oil (blue). (Image credit: Wiki commons, Creative Commons Attribution ShareAlike 3.0).
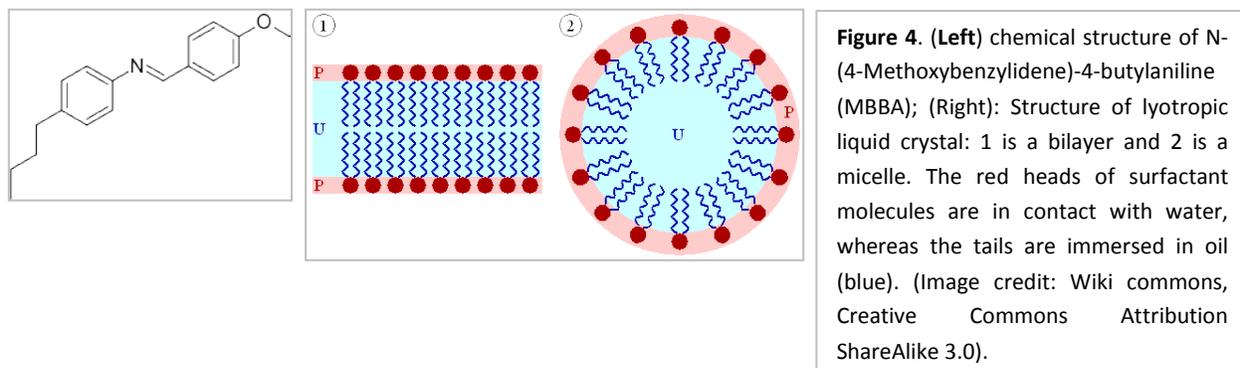
Lyotropic liquid-crystalline phases are **abundant in living systems**, such as biological membranes, cell membranes, many proteins (like the protein solution extruded by a spider to generate silk), as well as tobacco mosaic virus. Soap is another well known material which is in fact a lyotropic LC. The thickness of the soap bubbles determines the colours of light they reflect.

LCs applications

The order of liquid crystals can be manipulated with mechanical, magnetic or electric forces. What is interesting is that this change of order can be obtained with very small variations of these forces. The properties of liquid crystals are useful in many applications. The colour of some liquid crystals depends on the orientation of its molecules, so any perturbation that disturbs this orientation (e.g. a difference in magnetic or electric field; a difference in temperature; or the presence of certain chemicals) can be detected with a colour change.

EXPERIMENT B in the Experiment Module deals with synthesising and testing different temperature sensitive liquid crystals. In this experiment students test how different LCs are sensitive to different temperature ranges and build an LC thermometer.

The details of how a thermotropic LC works are described in the **background document** for **EXPERIMENT B in the Experiment Module**.

Liquid crystals are routinely used in **displays** for cell phones, cameras, laptop computers and other electronics. In these displays, an electric field changes the orientation of the molecules in the liquid crystal, and affects the polarisation of light passing through them. Because of their sensitivity to

temperature, and the property of changing colour, they are also used in thermometers. In miniaturised sensors, liquid crystals can detect certain chemicals, electric fields and changes in temperature.

Liquid crystal displays (LCDs) are discussed in **Chapter 4 of Module 2 "Applications of Nanotechnologies: ICT"**.

In the future LCs might have very interesting applications. Recently, it has been found that the inclusion of specific molecules, often in the order of nanometres, in the liquid crystal can lead to new electrical and optical properties in the LC. For instance, LC materials have been modified to induce new photonic functions, for application to waveguide and optical storage (ICT application area). Another class of LCs under development is photoconductive LCs, with the aim of having new materials for PVs cells and light emitting diodes (Energy application area). Another area of study is to modify LCs in ways that allow them to be used in stimuli-responsive materials and as templates for nanoporous polymers (potential nanomedicine application area).

Nanostructured Metals and Alloys

This section covers metal nanoparticles – nanocrystalline materials consisting of a single metal or of alloys made of two or more metals and nanostructured metal surfaces.

Metal nanoparticles

Metal nanoparticles are a clear example of how at the nanometre scale the properties of matter can change. For instance metal gold is notably yellow in colour and used for jewellery. As the noblest of all metals, gold is very stable (for instance, it does not react with oxygen or sulphur). However, if gold is shrunk to a nanoparticle, it changes colour, becoming **red if it is spherical** (**Figure 6**) and

Figure 6. Gold colloid is ruby red, not golden! (Image credit: L. Filipponi, iNANO, Aarhus University, Creative Commons Attribution ShareAlike 3.0).

even **colourless if it is shaped in a ring**. Moreover, gold nanoparticles become very reactive and can be used as **new catalysts** (this will be discussed in **Chapter 2 "Applications of nanotechnologies: Environment" of Module 2**).

Plasmonic structures

Noble metal nanoparticles, meaning gold, silver, platinum and palladium nanoparticles, show localised surface plasmon-resonances (LSPR), an effect that was described in **Chapter 4 of Module 2 ("Fundamental 'nano-effects'")**. **The energy of the LSPR depends on the particle shape, size, composition, inter-particle spacing and dielectric environment**. The surface of the nanoparticles can be functionalised with numerous chemical and biochemical molecules enabling specific binding of organic molecules such as antibodies, making them useful in **sensors** .

For this reason they are of special interest for optical detection and sensing in analytical chemistry and molecular biology. The refractive index can be used as the sensing parameter: changes in the local dielectric environment, induced by the sensing process, are used to detect the binding of molecules in the particle nano-environment. The change in aggregation between the nanoparticles as a result of analyte attachment affects the LSPR energy, so this effect can be used for highly miniaturised sensors. **Figure 7** schematically illustrates these two LSPR-based detection methods.
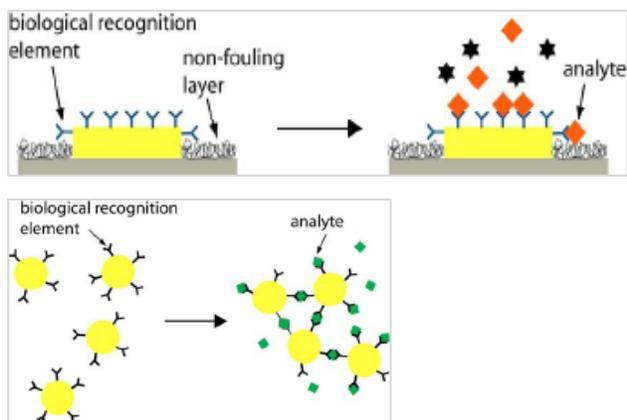
Figure 7. (Top) LSPR sensor based on a change of refractive index induced by analyte attachment on a functionalised surface; (Bottom) LSPR sensor based on a change in nanoparticle aggregation induced by attachment on functionalised nanoparticles.

Localised surface plasmons have been explored in a range of nanoparticle shapes such as disks, triangles, spheres and stars. Also more complex structures have been studied, such as holes in thin metal film, nanoshells and nanorings. Based on nanostructured metallic surfaces a variety of optical applications are possible. An important feature of plasmonic structures is that they allow label-free detection, which is important in optical sensing. Currently plasmonic components are being investigated with respect to future applications in cancer therapy, solar cells, waveguides, optical interconnection, camera LEDs, OLEDs and more.

The application of metal nanoparticles in medical diagnostics and targeted treatment is discussed in detail in **Chapter 1 of Module 2 "Applications of Nanotechnologies: Medicine and Healthcare"**.

Reinforcements

Metal nanoparticles are used as **reinforcements in alloys for application in lightweight construction** within the aerospace sector and increasingly in the automotive sector. The method is used for instance to harden steel. For instance, titanium nanoparticles are used as alloy compound to steel, and the resulting material shows improved properties with respect to robustness, ductility, corrosion and temperature resistance. Particles of iron carbide are also precipitated into steel to make it harder. The nanoparticles block the movement of the dislocations in the crystalline material (this effect was described in details in **Chapter 4 of Module 1 "Fundamental 'nano-effects'"**) increasing hardness. The trade off between steel strength and ductility is an important issue, since modern construction requires high strength whereas safety and stress redistribution require high ductility. The presence of hard nanoparticles in the steel matrix could lead to a material with a combination of these properties, effectively matching high strength with exceptional ductility.

Environmental applications

Some forms of metal nanoparticles have important environment applications.

➢ **Zero-valent (Fe0) iron nanoparticles** are under investigation for the remediation of contaminated groundwater and soil. Iron when exposed to air oxidises easily to rust; however, when it oxidises around contaminants such as trichloroethylene (TCE), carbon tetrachloride, dioxins, or PCBs, these organic molecules are broken down into simple, far less toxic carbon compounds. Iron nanoparticles are more effective than conventional 'iron powder', which is already used to clean up industrial wastes. Iron nanoparticles are 10 to 1000 times more reactive then commonly used iron powders.

➢ **Silver nanoparticles** have a strong anti-bacterial capacity. They are used in numerous products to prevent or reduce the adherence of bacteria to surfaces.

Metal nanoparticles and their use in environment applications are covered in the **Chapter 2 of Module 2 "Applications of Nanotechnologies: Environment".**

Nanocrystalline metals

Nanocrystalline metals are classical metals and alloys that have an ultra-fine crystalline structure below 100 nm. They exhibit **extraordinary mechanical and physical properties** which make them interesting for many applications. Examples of nanocrystalline metal materials are Al, Mg, and Al-Mg alloys which offer high strength and are lightweight. Other examples are Ti- and Ti-Al-alloys.

Some crystalline metals offer **exceptional magnetic properties**. An example is the "Finemet" nanocrystalline soft magnetic alloys, which consist of melt-spun Fe-Si-B alloys containing small amounts of Nb and Cu.

The application of nanomaterials in the field of magnetic materials is very important and promising, with applications in magnetic recording, giant-magneto resistance, magnetic refrigeration and magnetic sensing. These novel materials are composed of magnetic nanoparticles dispersed in a magnetic or nonmagnetic matrix (particle-dispersed nanocomposites) or of stacked magnetic thin films (magnetic multilayer nanocomposites).

We will cover the application of **nanostructured magnetic materials for memory storage** in **Chapter 4 of Module 2 "Applications of Nanotechnologies: ICT".**

Ferrofluids
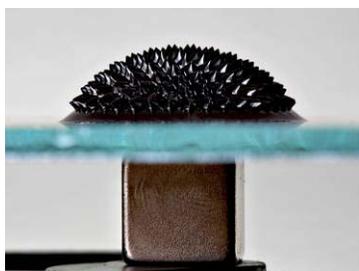
Figure 8 A ferrofluid with a magnet underneath. (Image credit: G. F. Maxwell, Wiki Commons, GNU Free documentation licence).

Ferrofluids are **colloidal mixtures composed of ferromagnetic or ferrimagnetic nanoparticles** (such as magnetite) suspended in a carrier fluid, usually an organic solvent or water. The ferromagnetic nano-particles are coated with a surfactant to prevent their agglomeration (due to van der Waals and magnetic forces). Although the name may suggest otherwise, ferrofluids do not display ferromagnetism, since they do not retain magnetisation in the absence of an externally applied field. Rather they display bulk-like paramagnetism, and are often referred to as "superparamagnetic" materials due to their large magnetic susceptibility. When a paramagnetic fluid is subjected to a sufficiently strong vertical magnetic field, the surface spontaneously forms a regular pattern of corrugations; this effect is known as the normal-field instability (**Figure 8**).

Ferrofluids have **numerous applications**: in mechanical engineering, particularly for vehicle suspension and breaking systems, due to their low-friction properties; in the ICT area, as liquid seals (ferrofluidic seals) around the spinning drive shafts in hard disks; and in the biomedical sector as drug carriers.

Polymers

A polymer is a large molecule made of a chain of individual basic units called monomers joined together in sequence. A copolymer is a macromolecule containing two or more types of monomers. When the polymer is a good conductor of electricity, it is referred to as conductive polymer (or organic metal). In this section nanostructuring of polymers and the effect this can have on polymers´ properties are described. The focus is on co-polymers since these are extremely useful in nanotechnologies.

Conductive Polymers

Polymers that are good conductors of electricity are called conductive polymers and include polyacetylene, polyaniline, polypyrrole, polythiophene and many more have been synthesised. These polymers are characterised by having alternating double-single chemical bonds, so they are π-conjugated. The π-conjugation of the carbon bonds along the oriented polymer chains provides a pathway for the flow of conduction electrons, and is thus responsible for the **good electrical conduction properties of the material**. A detailed SEM analysis of conductive polymers has revealed that these are made of a sequence of metallic nanoparticles about 10nm in diameter. **The high conductivity of polymers such as polyacetylene and polyaniline is related to the nanostructure of the polymer**. Polyaniline and its analogues **change colour** when a suitable voltage is applied, or when reacting with specific chemicals (electrochromic and chemochromic). For this reason they are promising for use in light-emitting diodes (LEDs). Other applications are the surface finish of printed-circuit boards, corrosion protection of metal surfaces, semitransparent antistatic coatings for electronic products, polymeric batteries and electromagnetic shielding.

Block Copolymers

A copolymer is a macromolecule containing two or more type of monomers, and a block copolymer has these basic units or monomer types joined together in long individual sequences called blocks. An example is the diblock polymer (A)m(B)n, which is made of a linear sequence of m monomers of type A joined together to a linear sequence of n monomers of type B. A transition section joints the two blocks:

[end group]-[polyA]m-[transition member]-[polyB]n-[end group]

Often, block copolymers are made of a **hydrophilic (water-attracted) block, and a hydrophobic (water-repellent) block**. In general, macromolecules having hydrophilic and hydrophobic regions, such as lipids, **self-assemble in ordered structures when in water**: the hydrophobic region packs together, avoiding the water molecules, leaving the hydrophilic molecules to the exterior of the structure. In the same way, block copolymers made of hydrophilic and hydrophobic blocks when mixed in a selective solvent, like water, can self-assemble into ordered architectures in the nanoscale regime.
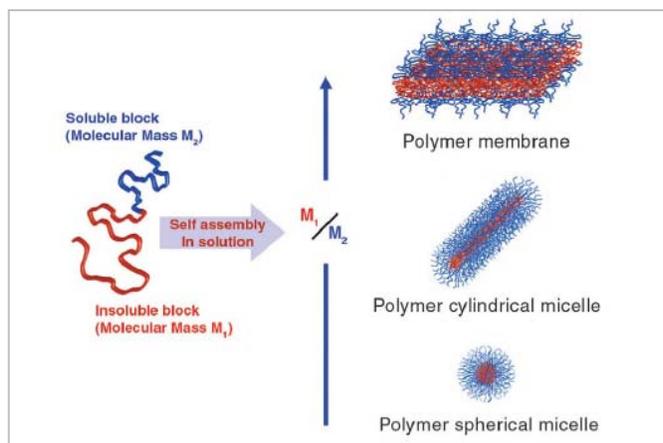
Figure 9. Different geometries formed by block copolymers in selective solvent conditions. Image adapted from Smart et al. Nano Today (2008), 3 (3-4), 38-45, Copyright (2008) with permission from Elsevier.

The geometry and degree of order of these structures depends on the concentration and the volume ratio between insoluble and soluble blocks. Depending on these parameters, the block copolymer can form **spherical micelles (nanospheres), cylindrical micelles and membranes**. Both cylindrical and spherical micelles consist of a nonsoluble (hydrophobic) core surrounded by a soluble corona. Membranes are made of two monolayers of block copolymer aligned to form a sandwich-like membrane: soluble block-insoluble block-soluble block. Molecules that at low concentration form spherical aggregates will assemble into cylindrical and eventually membrane-like structures as the concentration is increased (**Figure 9**).

Among spherical micelles, if the lengths of the projections formed by the hydrophilic corona are short compared to the sphere diameter, the nanostructure is called a "hairy nanosphere", whereas if the sphere is small and the projections long, it is called a "star polymer" (**Figure 10**).

Figure 10. Sketch of a star polymer and a hairy polymer. (Image credit: L. Filipponi, iNANO, Aarhus University, Creative Commons Attribution ShareAlike 3.0).

Star polymer   Hairy Nanosphere
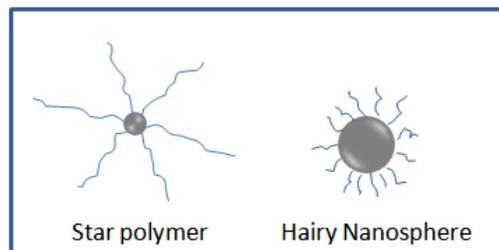
Responsive "smart" polymers

Block copolymers form nanostructures that are **very sensitive to external fields**. For instance moderate electrical fields or shear stimulation can trigger macroscopic re-arrangements in specific directions. This is a versatile property for making **materials that respond and change on demand**. The intrinsic macromolecular nature of these copolymers leads to very slow and kinetically controlled phase transitions. Thus metastable or intermediate phases have longer lifetimes, which is desirable in applications that want to exploit the phase transition properties of these materials.

Biomedical applications

The ability of block copolymers to form nanoparticles and nanostructures in aqueous solutions makes them particularly useful for biomedical applications, such as therapeutics delivery, tissue engineering and medical imaging. In the field of **therapeutic delivery**, materials that can encapsulate and release drugs are needed. Hydrogels are very useful for the controlled release of drugs and block copolymer hydrogels are particularly advantageous for the possibility of conferring some stimuli-activated properties, such as temperature-sensitivity. Block copolymers form nanostructures with both hydrophilic and hydrophobic areas, so they can form vesicles that can encapsulate and carry both hydrophobic and hydrophilic therapeutic agents. Micelles formed using block copolymers have a hydrophilic corona that makes them more resistant to the interaction of proteins, in particular plasma proteins; therefore these types of micelles exhibit long circulation times *in vivo*. Insoluble domains can also be engineered to exploit the sensitivity of specific hydrophobic polymers to external stimuli such as pH, oxidative species, temperature and hydrolytic degradation.

Block copolymers are also of interest for preparing **scaffolds for tissue engineering**. For instance very long micelles that mimic the natural extracellular have recently been prepared exploiting the self-assembly properties of a peptide copolymer.

Nano-reactors

The ability to generate **compartmentalised volumes at the nanometre level** is one of the fundamental mechanisms used by cells in synthesising biomolecules and performing the biochemical processes necessary for their function. This motif is now reassembled using block copolymer micelles and vesicles as **nanoreactors**. This approach has been employed for carrying enzymatic reactions in nanosized compartments.

It has been shown that this approach can also be expanded into a nonaqueous solvent. For instance a recent work reports block polymer nanostructures in ionic liquid and the ability of micelles to shuttle from an aqueous solvent to an ionic liquid as a function of temperature. This opens the way to using block copolymer technology in more sophisticated synthetic routes.

Artificial moving parts

Block copolymers structures can also be used to mimic the ability of biomolecules to convert chemical energy into mechanical energy, for instance by using a pH sensitive block copolymer whose micelles swell according to pH variation. Thus these materials are being investigated to create artificial muscles or moving nanostructures.

Other applications

The application of block copolymers is not limited to the biomedical field. They can be used in conjunction with other materials to form block copolymer nanocomposites. For instance star polymers are used in industry to **improve metal strength**.

Finally, block copolymers can form nanoporous membranes for applications in f**iltering systems and fuel cell technology**.

Polymeric nanofibres

Nanostructured fibrous materials, or **nanofibres**, are an important class of nanomaterials, now readily available thanks to recent developments in electrospinning and related fabrication technologies. In contrast to conventional woven fabrics, they have the typical structure illustrated in **Figure 11.**
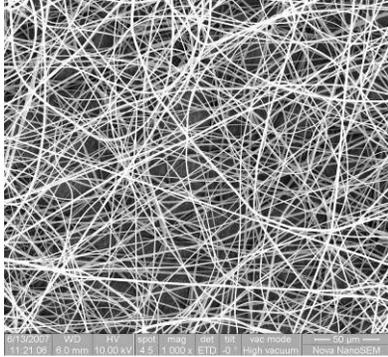
Figure 11. A typical sample of electrospun polystyrene. (Image credit: T. Uyar, Interdisciplinary Nanoscience Canter (iNANO), Aarhus University. Copyright 2008. Reprint not permitted).

Nanofibres have some unique properties: they are highly porous, i.e., they have a large interconnected void volume in the range of 50% or even greater than 90% and possess a very high surface-to-volume ratio. It is possible to increase the mechanical stability of nanofibrous structures by annealing the fabric so to join together the crossing points of those fibres.

These properties make nanofibrous scaffolds useful for many biomedical and industrial applications.

In addition, researchers have succeeded in making **coaxial nanofibres composed on two different polymers** or composite coaxial fibres. Researchers are also trying to make **aligned nanofibres**. These types of materials, particularly if made of conducting polymers, could have important applications for electronic and medical devices.
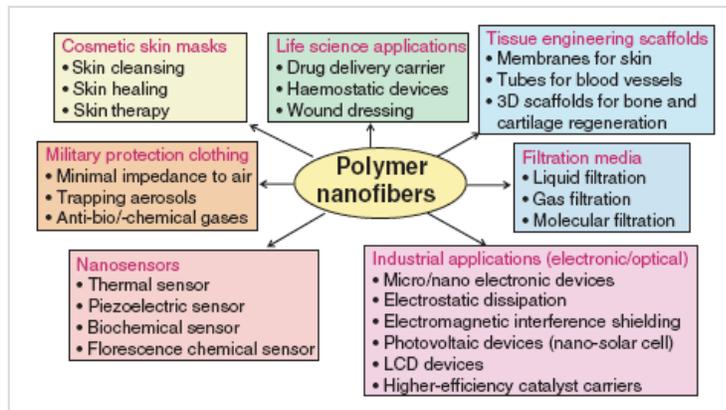
Nanofibres have a **broad spectrum of applications** as schematised in **Figure 12**.

Figure 12. Overview of polymer nanofibres applications.

The two areas that have so far received most attention are the **medical field** (e.g. wound healing membranes) and **filtration applications**. These will be covered in **Chapter 1 "Applications of nanotechnologies: Medicine and healthcare"** and **Chapter 2 "Applications of nanotechnologies: Environment" of Module 2** respectively). Nanofibres are also being considered for composite material reinforcement. As nanofibres are a relatively recent type of nanomaterial it is expected that in the future many more applications will be explored.

Semiconductors

Semiconductors, unlike metals, have a band gap. The band gap is between the valence band and the conduction band. In intrinsic semiconductors which possess no impurities (like boron, silicon, germanium, indium) there are no electronic states in the band gap. The properties of semiconductors, in particular the band gap, are manipulated by addition of dopants – impurities able to donate charge carriers in the form of electrons (n-type) or holes (p-type).

As with metals, the reduction of the size of the semiconductor triggers the insurgence of novel physical properties. The most evident example is that of quantum dots.

Quantum dots

Quantum dots are made of semiconductor materials such as CdSe, ZnSe, CdTe, about 10 nm in size. As in the case of metal nanoparticles, electrons in quantum dots are localised in space.

Figure 13. Ten distinguishable emission colours of ZnS-capped CdSe QDs excited with a near-UV lamp. From left to right (blue to red), the emission maxima are located at 443, 473, 481, 500, 518, 543, 565, 587, 610, and 655 nm. (Reprinted by permission of Macmillan Publishers from Macmillan Publishers Ltd: Nature Biotech. (2001) 19, 631-35, Copyright 2001).

A QD has a discrete quantised energy spectrum, so it can absorb a specific wavelength and emit a **monochromatic colour**. Depending on their size, **QDs emit different colours**, as shown in **Figure 13**. The reason for this was explained in **Chapter 4 of Module 2 ("Fundamental 'nano-effects'")**: the width of the bandgap is related to the size of the semiconductor; smaller sizes lead to a blue shift in the emission spectra.

QDs, like metal nanoparticles. hold great promise for nano-enhanced imaging which will bring progress to fields like environmental monitoring, medical diagnostics and treatment. QD are also being investigated as novel light sources to improve LED technology and in solar cell technology. These applications of QDs in the energy and ICT sectors will be reviewed in **Chapter 3 "Applications of Nanotechnologies: Energy" and Chapter 4 "Information and Communication Technologies" of Module 2.**

Semiconducting oxides

Semiconducting oxides like TiO_2 and ZnO in bulk (macro) form are widely used in industry in many products. When they are in a nanoscale form, they display interesting physical properties that allow the designing of new materials and the improvement of old ones. Below is a short description of these properties.

Titanium dioxide

Titanium dioxide (TiO_2) is a mineral mainly found in two forms, rutile and anatase. Titanium dioxide is the most widely used white pigment because of its brightness (white colour) and very high refractive index (n=2.4). It is used in paints, plastics, toothpastes, papers, inks, foods and medicines. In sunscreens with a physical blocker, titanium dioxide is used both because of its high refractive index and its resistance to discolouration under ultraviolet light. This is because TiO_2 is a UV filter, it absorbs UV light. TiO_2, particularly in the anatase form, can be employed also as a photocatalyst under UV light. It oxidises water to create hydroxyl (OH) radicals and it can also oxidise oxygen or organic materials directly. For this reason TiO_2 is added to confer sterilising, deodorising and anti-fouling properties to paints, cements, windows and tiles.

Titanium nanoparticles (30-50nm, often referred to as **nano-TiO₂**) are at the centre of much attention due to their optical and catalytic properties: they retain the ability to absorb UV light but light scattering is dramatically reduced, so that TiO_2 goes from appearing white to transparent (a detailed explanation of this effect is given in **Chapter 4 of Module 1 ("Fundamental 'nano-effects'")**. **Nano-TiO₂** is thus suitable for transparent coatings, and for new generation sunscreens, which are characterised by a high protective factor but transparent appearance. The catalytic properties of TiO_2 when in a nano-size are also greatly enhanced by the large surface-to-volume ratio. This property is increasingly used for chemical catalysis applications such as photo-catalytic purification of water and air to decompose organic pollutants (solar photocatalytic remediation). Thin films of TiO_2 are used in windows to confer self-cleaning properties on the glass (This application of nano-TiO₂ nanoparticles is reviewed in the **"Nanocoatings"** section of this document).

ELSA & SATETY TOPIC: The use of nanoparticles in sunscreen is under much attention because some environmental organization, like Friends of the Earth Australia, have accused that the nanoparticles used in these products can pass the skin barrier and enter the blood stream, causing unwanted harm. To support this statement they refer to research published on the toxicity of nano-titanium and nano-zinc oxide. These studies though often use amounts and exposure conditions (e.g., injection or inhalation) which are very different from what consumers of these sunscreens would be exposed to (cream rubbed on skin, amount and frequency of use, skin washed after some time, sun exposure, etc.). Manufactures claim that the nanoparticles used in the sunscreen formula are agglomerated; therefore they have dimensions that don't allow for skin-penetration. Reseach seem to support this statement. Opponents reply that long term studies must be performed before this can be demonstrated, and that skin types vary from person to person, not to mention cases of damaged skin, so generalizations are not possible yet (studies are mainly done *in vitro* using healthy skin). Overall, more research is called upon by all stakeholders, including regulators, to establish the safety of these products.

NANOYOU DILEMMA The example titanium dioxide in sunscreens is used in one of the NT Virtual Dialogue debates (see www.nanoyou.eu/en/decide). In this dilemma students consider the case of sunscreens with nanoparticles and reflect on their advantages and possible disadvantages.

Another important application of nano-TiO2 is in **organic solar cells**, like the Grätzel solar cell, where nano-TiO$_2$ is used as the catalyst to promote light-induced electrical charge separation. The use of titanium dioxide in this type of solar cells is covered in more detail in **Chapter 2 "Applications of Nanotechnologies: Environment" of Module 2**.

One limitation of using TiO$_2$ as a photocatalyst is that this material **only absorbs UV light**, which represents about 5% of the solar spectrum. In this context, nanotechnology could bring an improvement in the form of nanoparticles with surfaces modified with organic or inorganic dyes to expand the photoresponse window of TiO$_2$ from UV to visible light.

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Zinc dioxide

Zinc oxide (ZnO) has some similar properties to TiO_2, i.e., its nanoparticles scatter light so it can be used for transparent UV filters, in creams or coatings. Like TiO_2 it is used for solar photocatalytic remediation but compared to TiO_2 it has a weaker photocatalytic effect. ZnO also suffers from the same limitation of absorbing only a fraction of the solar spectrum so research is underway to increase its photoresponse.

A peculiarity of ZnO is that it has a tendency to grow in **self-organised nanostructures**. By controlling crystal growth conditions, a variety of crystal shapes are possible. Researchers have been able to grow nanoscale wires, rods, rings etc. ZnO nanocolumns are of particular interest since low-temperature photoluminescence measurements have revealed intense and detailed **ultraviolet light emission** near the optical band gap of ZnO at 3.37 eV. ZnO thus can act as an optical amplification medium and as a laser resonator.

ZnO wires arrayed on a surface are also being investigated as piezoelectric elements for **miniaturised power sources**. This would allow creating flexible, portable power sources that could be included in textiles so that they are able to scavenge energy from body motion, light wind, air flow etc .
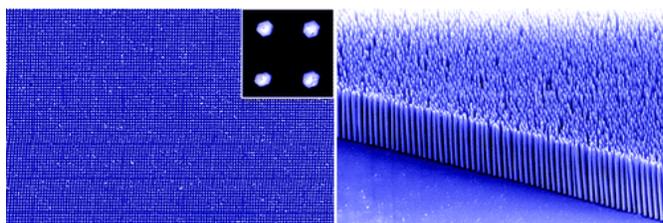

Figure 14. Patterned ZnO grown as vertical pillars in an arrayed format. (Reprinted with permission from Xu et al., Journal of American Chemical Society 2008, 130, 14958-14959. Copyright 2008 American Chemical Society.

The use of ZnO for the development of miniaturised power sources is described in detail in **Chapter 3 of Module 2 "Applications of Nanotechnologies: Energy"**.

ITO

ITO is a semiconducting material whose main feature is the **combination of electrical conductivity and optical transparency**. ITO is made of around 90% indium(III)-oxide (In_2O_3) and around 10% tin(V)-oxide (SnO_2). It is widely used in its thin-film form as transparent electrodes in liquid crystal displays, touch screens, LEDs, thin-film solar cells, semiconducting sensors, etc. ITO is an **infrared absorber** so it is now used as a thermal insulation coating on window glass. Its anti-static properties make it additionally useful in applications like packaging and storage of electronic equipment. Since the material is very expensive, alternative materials, such as fluor tin oxides and aluminium zinc oxides are being considered. The use of ITO in "smart coatings" is further discussed in the **"Nanocoatings"** section of this document.

Photonic crystals

A photonic crystal consists of a lattice of periodic dielectric or metal-dielectric nanostructures that affects the propagation of electromagnetic waves. Essentially, photonic crystals contain regularly repeating internal regions of high and low dielectric constant. Photons (behaving as waves) propagate through this structure – or not – depending on their wavelength. The periodicity of the photonic crystal structure has to be of the same length-scale as half the wavelength of the electromagnetic waves, i.e. ~200 nm (blue) to 350 nm (red) for photonic crystals operating in the visible part of the spectrum. Such crystals have to be artificially fabricated by methods such as electron-beam lithography and X-ray lithography.

Photonic crystals exist in Nature. For instance in **Chapter 2 of Module 1 "Natural Nanomaterials"** it was shown how the beautiful blue wings of some butterflies owe their colour to their internal nanostructure, which is in fact a photonic crystal structure.

Photonic crystals are now receiving much attention because of their potential in particular in the **optical-communication industry**. Researchers are considering using **light and photonic crystals** (in alternative to electrons travelling in wires) for the new generation integrated circuits. Light can travel much faster in a dielectric medium than an electron in a wire, and it can carry a larger amount of information per second. Given the impact that semiconductor materials have had on every sector of society, photonic crystals could play an even greater role in the 21st century. Photonics and their impact in the ICT sector are analysed in **Chapter 4 of Module 2 ("Application of Nanotechnologies: ICT")**.

Ceramic and glassy materials

Ceramic materials by definition are ionically bound; they are hard materials, both electrically and thermally very stable. In this category are included for instance Al_2O_3, Si_3N_4, MgO, SiO_2, Na_2O, CaO, and ZrO_2. Ceramics are characterised by being **hard yet brittle**, therefore in many cases they are used as **composites** where they are mixed with other materials (e.g. metals) to increase their mechanical performance. Composite hard nanocoatings are particularly important for cutting tools (see the section **"Inorganic composites"** in this document).

Ceramics exist both in a crystalline and non-crystalline form (for instance the broad family of "glass"). Nanostructures within the material have important consequences for their properties, as discussed in the next sections.

Porous alumina

Porous alumina membranes produced by anodic aluminium oxidation are characterised by having hexagonally close-packed channels with diameters ranging from 10nm to 250 nm or greater. This material is often used as a **template** for the synthesis of other materials.

Zeolites

Zeolites are natural crystalline materials with pores having regular arrangements. They are also often used in the template synthesis of nanomaterial. They can also be used to prepare organised structures of a certain material to confer new optical properties on it. For instance, selenium can be incorporated into the channels of mordenite, a natural zeolite. The difference between a mordenite-selenium crystal and a natural selenium crystal is noteworthy: the optical absorption spectrum is considerably shifted to higher energies for the mordenite-selenium crystal.

Figure 15. A schematic representation of a zeolite. (Image credit: Wikimedia Commons, image for public domain).
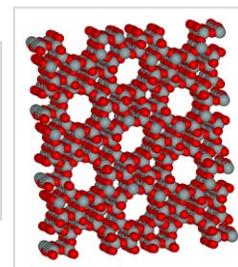
Aerogels

Silicon dioxide (SiO_2) is the main component of quartz. It is chemically robust and finds widespread applications. In commercial products it appears as an additive in rubber products for vehicle tyres but it is also the component of new types of aerogels. Generally speaking an aerogel is a solid with up to 95% of the volume consisting of nanoscale pores. Aerogels are manufactured with a sol-gel technique and can be made of carbon, metal oxide, polymers or silicates.

Figure 16. The thermal insulating properties of a silica aerogel. (Image credit: Wikimedia Commons, image for public domain).

Due to their **high porosity** aerogels have an extremely high surface area and very low thermal conductivity. Thus they are suitable for **thermal insulation and as filter materials** (**Figure 16**). Another prominent property is their low specific weight, making them interesting for **lightweight construction**. Aerogels are also interesting for their optical properties, namely **high optical transparencies**. Silica aerogels are made of pores of about 10 nm arranged in distances between 10 and 100nm. They are resistant and chemically inert to liquid metals, heat resistant up to 1200°C and non-toxic, thus they have also **biomedical applications**, such as substrates for cell growth and analysis. One of the problems of SiO_2 aerogels that needs to be addressed is that this material has to be expensively protected against humidity, since it is not water resistant and suffers from a loss of stability and thermal conductivity once it gets wet.

Carbon-based materials

In Nature there are some pure materials that have striking different properties even though they are made of the same atoms. For instance, **graphite** and **diamond** (**Figure 17**): two very popular materials, one used conventionally in pencils and the other in jewellery. These two materials could not be more different: graphite is soft, light, flexible, and conducts electricity while diamond is extremely strong, hard and does not conduct electricity. Both materials are made of atoms of carbon linked through strong bindings (covalent), but in graphite each carbon atom uses three out of its four electrons to form single bonds with its neighbours, forming a linear sheet, whereas in diamonds each carbon atom uses all its four electrons to form four single bonds, resulting in a 3-D structure. The different properties of graphite

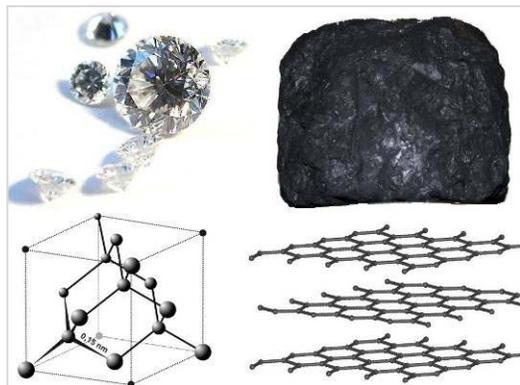and diamond are a consequence of the different way the carbon atoms in the materials are bonded together.

Figure 17. Two allotropes of carbon and their respective chemical structure: (left, top and bottom): diamond; right (top and bottom): graphite.(Image credit: Wiki Commons, Creative Commons Attribution ShareAlike 3.0)

Graphite and diamond are two pure forms (**allotropes**) of carbon. In 1985 a new allotrope of carbon was discovered formed of 60 atoms of carbons linked together through single covalent bonds arranged in a highly symmetrical, closed shell that resembles a football. This material was officially named Buckminsterfullerene and is often referred to as buckyball, fullerene or simply C_{60}. Since its discovery, fullerenes with 70, 80 and even more carbon atoms have been discovered.

In the early 1990s, an incredible new carbon form was discovered, carbon nanotubes. These appear like graphite sheets rolled up with fullerene-type end caps, but have totally different properties compared to graphite. **Figure 18** shows different forms of carbon allotropes (image d and h are structures of a C_{60} and a nanotube, respectively).
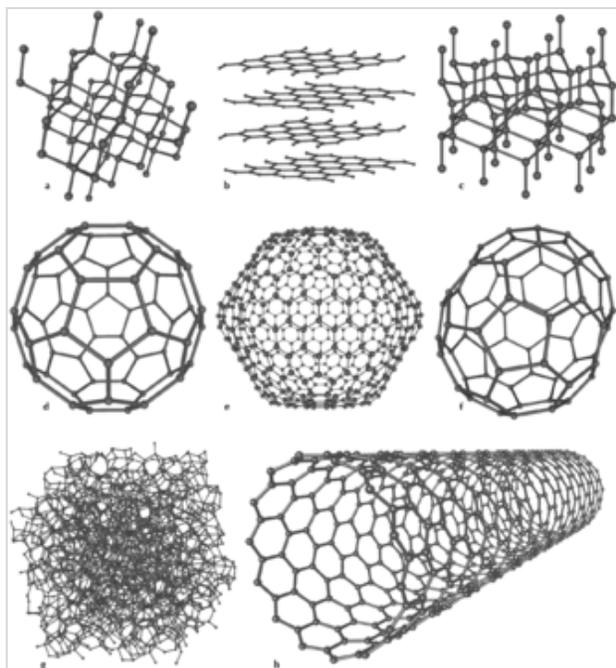
Figure 18. Eight allotropes of carbon: (a) diamond, (b) graphite, (c) lonsdaleite, (d) C60, (e) C540, (f) C70, (g) amorphous carbon and (h) a carbon nanotube. Image by Michael Ströc, (GNU Free Documentation License).

It is now known **that fullerenes and carbon nanotubes form naturally in common places like flames** (produced by burning methane, ethylene and benzene) and in soot. Scientists have now developed methods to synthesise these

nanomaterials with control over their final properties.

Carbon nanotubes

Carbon nanotubes can appear as single-wall nanotubes (SWNTs), with a diameter of approximately 1.4nm, or multi-wall nanotubes (MWNTs), consisting of 2 to 30 concentric tubes with an outer diameter of 30-50nm. The structure of an SWNT can be conceptualised by wrapping a one-atom-thick layer of graphite called graphene into a cylinder. To complete the nanotube, imagine adding two half fullerenes on each end of the nanotube.

Carbon nanotubes can range in length from a few tens of nanometres to several micrometers, and can have metallic properties (comparable to or even better than copper) or can be semiconductors (like silicon in transistors), depending on their structure. These nanomaterials are truly amazing and have great potential in numerous fields as illustrated in **Figure 19**.

Figure 19. Overview of application areas of carbon nanotubes. (Reprinted from: M.A.H. Hyder, Master Thesis, Technical University of Hamburg-Harburg, Germany, Copyright M. A. H. Hyder 2003).
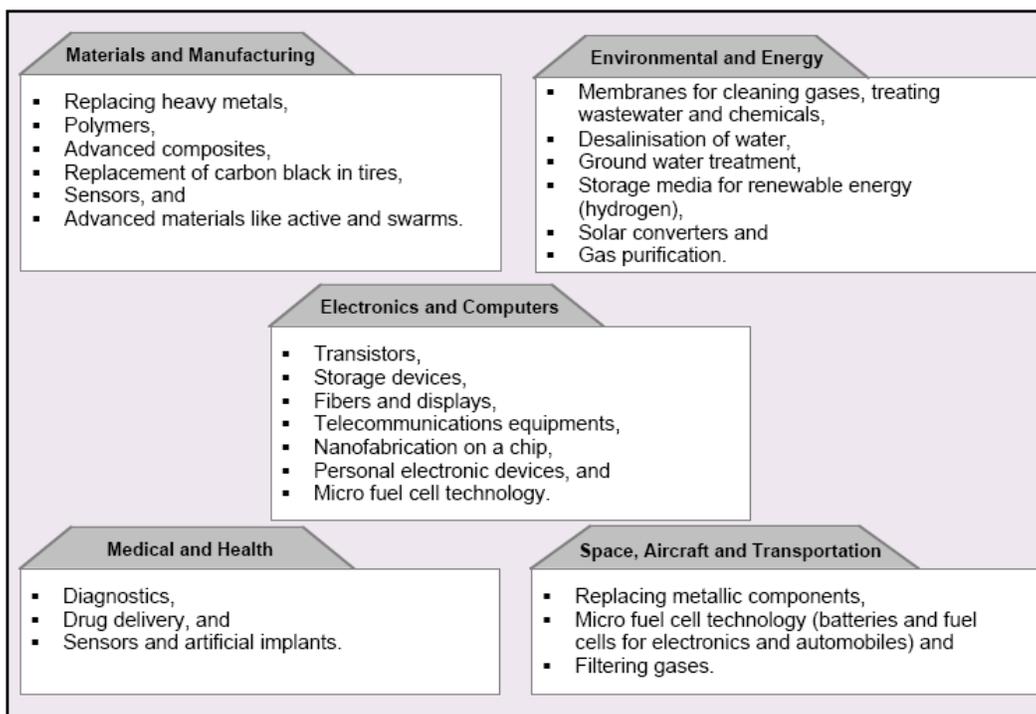
The application of CNTs in the energy, environment, medicine and ICT sectors are covered in the respective application chapters in **Module 2**.

Mechanical properties

The chemical bonding of nanotubes is composed entirely of sp^2 bonds (carbon double bonds) similar to those of graphite (whereas in diamonds all bonds are sp^3). This bonding structure, which is stronger than the sp^3 bonds found in diamonds, provides the molecules with their **unique strength**. Nanotubes naturally align themselves into "ropes" held together by Van der Waals forces.

Theoretical predictions say that carbon nanotubes are 100 times stronger than steel but have one sixth of its weight. Therefore they are ideal in lightweight construction, for instance for the automotive and aviation industries. Carbon nanotubes are already used in some consumer products to add strength (without compromising weight) such as tennis rackets.

The mechanical properties of carbon nanotubes are summarised in the table below. **Young's modulus** is a measure of how stiff, or elastic, a material is. The higher the value is, the less a material deforms when a force is applied. **Tensile strength** describes the maximum force that can be applied per unit area before the material snaps or breaks. A third interesting measure of a material is its **density**, which gives an idea of how light a material is. From the table below it can be seen that wood is very light but weak, while nanotubes are many times stronger than steel and yet much lighter.

Material	Young´s Modulus (GPa)	Tensile Strength (GPa)	Density (g/cm3)
Single-wall nanotube	800	>30	1.8
Multi-wall nanotube	800	>30	2.6

Diamond	1140	>20	3.52
Graphite	8	0.2	2.25
Steel	208	0.4	7.8
Wood	16	0.008	0.6

Table 1

Because of their mechanical properties carbon nanotubes are very interesting as fillers in **polymeric and inorganic composites**.

Electrical and thermal properties

The electrical properties of a material are based on the movement of electrons and the spaces or "holes" they leave behind. These properties are based on the chemical and physical structure of the material. In nanoscale materials some interesting electrical properties appear. Carbon nanotubes are the best example of this effect at the nanoscale. If one considers "building" a nanotube by rolling up a graphene sheet, the resulting nanotube can be conductive (and indeed, very conductive!) or semiconductive with relatively large band gaps. The electrical properties of the nanotube depend on the way it was "rolled up" (technically known as chirality). If it is rolled up so that its hexagons line up straight along the tube's axis, the nanotube acts as a metal (conductive). If it is rolled up on the diagonal, so the hexagons spiral along the axis, it acts as a semiconductor.

Why is this so? Graphene (that is, one layer of graphite) is not an insulator, but also neither a metal nor a semiconductor; it has electrical properties somehow in between, it is called a "semimetal". When rolled up, it leads to a structure that is either metallic or semiconducting. On the other hand diamond has a tetrahedral structure (derived from the fact that carbons are hybridised sp^3 rather than sp^2 as in graphene) and is an insulator.

One interesting property found in single-walled carbon nanotubes (SWCNT) is that electric conductance within them is **ballistic** (which means that all electrons that go into one end of the conductor come out of the other end without scattering, regardless of how far they need to travel).

Researchers are also investigating whether nanotubes can be **superconductors near room temperature**, meaning ballistic conductors that also exhibit a resistance of zero. A superconductor can transport an enormous amount of current flow at tiny voltages. At present known superconductors work at very low

temperatures. This field of research is very important since if a material were superconductive at room temperature, it would carry current with no resistance, with no energy lost as heat. This could lead to faster, lower-power electronics and the ability to carry electricity long distances with 100 per cent efficiency.

Nanotubes as superconductors and their applications are further discussed in **Chapter 3 "Applications of Nanotechnologies: Energy" of Module 2**.

In terms of thermal properties, carbon nanotubes **dissipate heat** better than any other known material and are **excellent thermal conductors**.

Chemical reactivity

Carbon nanotubes are very stable; they can withstand the attack of numerous chemicals and resist exposure to a large temperature range. However, their chemical structure can be changed by the addition of specific ligands with functional groups that allow interaction with different chemicals. This allows using them in **sensors**.

Applications

Carbon nanotubes are very promising materials for numerous applications (these will be described in more detail in **Module 2**). Applications include: nanomedicine (drug delivery), environment (chemical sensors), energy (supercapacitors, hydrogen storage materials, solar cells), ICT (integrated circuits, electronic paper), advanced materials for construction, transport, sports equipment and more.

ELSA & SATETY TOPIC: Carbon nanotubes are an extraordinary material which could improve numerous current materials, particularly some plastic composites, and be used in electronics and sensing. The range of application is fairly broad so the question of their safety is important. Carbon nanotubes are formed as nanometre thin, long fibres, so the memory quickly goes back to asbestos, their claimed exceptional properties, but also their late-found toxicity (they cause cancer). Some recent research does suggest that carbon nanotubes, inhaled in large amounts, can be significantly toxic. As with other nanomaterials, though, the question of safety is more complex: carbon nanotubes are used as composites, embedded with polymers or other materials, so consumers would not be directly exposed to them (with the exception of workers in industry). But what happens when the product is disposed and the material degrades? Is waste containing carbon nanotubes safe? Should this waste be treated differently and undergo special treatment? There is intense research to find answers to these questions, but time is needed. Opponents advocate that until these answers are not found, products containing carbon nanotubes should not be placed on the market, and workers should treat these as hazard materials and wear the stringiest protection measures.

> **NANOYOU GAME** *Carbon nanotubes composites are used in one of the NANOYOU Jigsaw puzzle game. Students need to match the nanomaterial, to its application, connecting it to a specific need. The game can be found at:*
> *http://nanoyou.eu/en/play-nano.html*

Scientists have now developed methods to control the synthesis of carbon nanotubes to obtain regular structures with specific properties. To date, though, the synthetic processes lead to moderate amount of CNTs and mostly very limited length (of the order of millimetres). Often these processes lead to CNTs which are not totally pure (traces of the catalyst used in the synthesis are present in the product) and this has been associated with toxicity issues of CNTs.

The cost associated with the production of carbon nanotubes is extremely high. In the future this cost must be considerably reduced to allow large-scale production and use of CNTs.

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, like **bone**, which is a hierarchical nanocomposite built from ceramic tablets and organic binders (see **Chapter 2 of Module 1 "Natural nanomaterials"**). 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 through the bulk material. The base material itself generally consists of non-nanoscale matrices. Nanocomposite typically consists 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 in the nanosize. 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 chapter, nanocomposites are sub-divided 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.

Inorganic nano composites

High-performance ceramics are sought in many applications, like highly efficient gas turbines, aerospace materials, automobiles 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 here we limit the review 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 incorporating a second phase such as particulates, platelets, whiskers, and 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 have 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 too much into the details, we list here some examples of inorganic **nanocomposites that have improved structural properties**:

> The incorporation of **fine SiC and Si$_3$N$_4$ nanoparticles in an alumina matrix** (Al$_2$O$_3$, a structural ceramic material) first demonstrated the concept of structural nanocomposites. The dispersion of these particles have shown to improve the fracture toughness from 3 to 4.8 MPa m1/2 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 Al$_2$O$_3$/W or MgO/Fe. **Granular films** can also be made with a ceramic phase embedded with nanosize metal granules (such as Fe/Al$_2$O$_3$, Fe/SiO$_2$). Such films often show **unusual or enhanced transport, optical and magnetic properties**. The inclusion of nanosized 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** (called metal matrix composites, or MMC). 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 with this method are particularly useful in the aerospace, automotive and aircraft industry. 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 MMC 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 α-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 (MMC) 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, e.g. 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 Nb and Cu. 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 10nm. These alloys have excellent magnetic induction and large permeability, and a very small coercive field.

Nanosized magnetic powders can have extreme properties and have no hysteresis at any temperature. These materials are called **superparamagnetic** and one example is nanosized 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. $Nd_2Fe_{14}B$). In these materials is has been found that the coercive field decreases significantly below ~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 $Nd_2Fe_{14}B$ and $Sm_2Fe_{17}N_3$, within soft magnetic matrices (e.g. soft α-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 20nm. 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 start contacting 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.

Magnetic multilayer nanocomposites are becoming an essential component of the **new generation data storage devices** like **Magnetoresistive Random Access Memory** (MRAM). This and other nanostructured devices made of nanomagnets with applications in the ICT sector are discussed in **Chapter 4 of Module 2 ("Applications of Nanotechnologies: ICT")**.

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, like heat resistance or mechanical strength, or to decrease other properties, like 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, light-weight 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 macro scale 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 100nm in at least one dimension. Nanoscale fillers include: nanoparticles; nanotubes; and layered (also called "plate-like") inorganic materials such as clays (**Figure 20**).
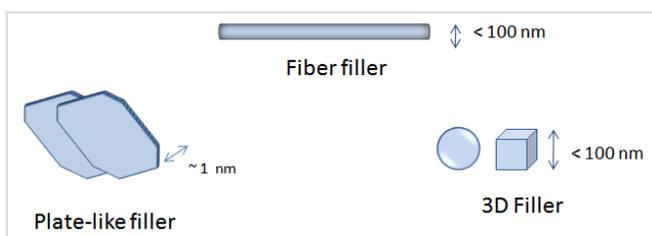

Figure 20. Schematic representation of nanoscale fillers. (Image credit: L. Filipponi, iNANO, Aarhus University, Creative Commons Attribution ShareAlike 3.0).

Although **some nanofilled composites have been used for more than a century**, such as carbon-black and fumed-silica-filled polymers, only recently have researchers 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 nanofillers, 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 nanofillers, a key requirement is the homogeneous dispersion of the filler within the polymer matrix. As will be discussed in the next 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 so far highest values of elastic modulus, as high as 1 TPa, and strengths that can be as high as 500 GPa. This could allow for instance 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 100nm 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 also, however, 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 with 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 nanofillers 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 Au 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, and this is discussed in a separate section of this chapter (see the section **"Polymers"**).

In terms of properties, the use of nanoparticles in filling polymers can influence not only the polymer mechanical properties, but also the **polymer mobility and relaxation behaviour**, which in turn are

connected with the glass transition temperature of the polymer (Tg), that is, the temperature at which a polymer becomes brittle on cooling or soft on heating. In general, adding well dispersed, exfoliated nanofiller increases the Tg 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 1** (page 29). In the context of nanocomposites, **SWNT are the most promising nanotube fillers**. Some properties are particularly interesting, in particular their **flexibility under mechanical stress**, their behaviour under high temperature conditions and their electrical properties. As with other applications that make use of carbon nanotubes, in composites it has been observed that the processing conditions ultimately affect nanotubes' properties, and as a consequence the composite, as well as the nanotubes' purity. Carbon nanotubes can also be doped, for instance 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 SWNT are in a bundle; until SWNT are isolated from the bundles or the bundles are crosslinked, the modulus of composites made from 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 for clay-polymer nanocomposites, the structural arrangement of the nanofiller 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 mechanical enhancement of polymers, **nanotubes are also of interest for their electrical properties**. **Carbon nanotubes are inherently more conductive then graphite**. It has been found for

instance that nanotube/PPV composites show a large increase in electrical conductivity compared to simple PPV, of nearly 8 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 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% in 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 about 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 called 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 few nanometres; in the exfoliated state the silicate layers are totally separated and dispersed in a continuous polymer matrix. Those two states are schematised in **Figure 21**.

Figure 21. Principle of formation of clay monolayer containing nanocomposites with enhanced mechanical and barrier properties. (Reprinted with permission from: Weiss, J.; Takhistov, P.; McClements, D. J., "Functional Materials in Food Nanotechnology". In Journal of Food Science 2006; Vol. 71, pp R107-R116. Copyright 2006 Wiley-Blackwell).
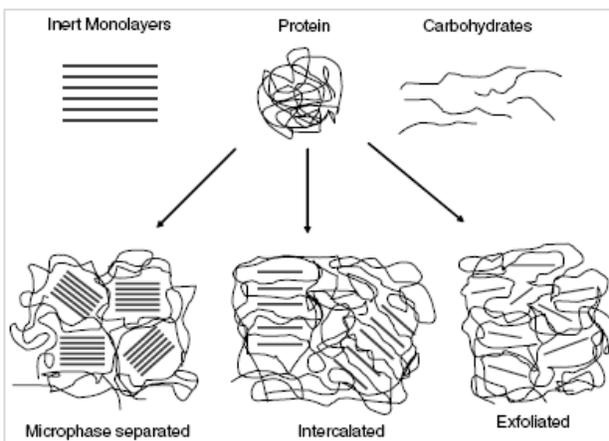
As mentioned before, the fabrication of a **polymer-clay nanocomposite requires mixing two components that are intrinsically non-compatible**. Surfactants are ionic, and thus interact well with the clay, but not with the polymer. An ideal solution is the use of "macro-surfactants" like block copolymers combining hydrophilic and hydrophobic blocks that can interact with the clay and the polymer respectively. For instance poly(ethylene oxide), or 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* (see **Chapter 2 of Module 1 "Natural Nanomaterials"** for details on the structure of bone). 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 ultrastrong and stiff layered polymer nanocomposites. In this work bottom-up assembly of clay/polymer 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 clay/polymer nanocomposites are also improved. Combining traditional flame retardants with intercalated or, better, exfoliated clays can result in further improvements in flame retardance.

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

Nanocoatings

Nanocoatings are a type of nanocomposites. The layer thickness of a nanocoating is usually in the 1-100 nm range. Nanocomposite films include multilayer thin-films, in which the phases are separated along the thickness of the film, or granular films, in which the different phases are distributed within each plane of the film (**Figure 22**).

Figure 22. Schematic of possible structures for nanostructured coatings. (Left) multilayered microstructure (e.g., TiN/TiC) for nanocomposite coatings; (right) homogeneous nanostructured coating (e.g., NiCoCrAlY alloy). (Image credit: L. Filipponi, iNANO, Aarhus University, Creative Commons Attribution ShareAlike 3.0).

Nanocoatings make it possible to **change properties of some materials**, for instance to change the transmission of visible and IR radiation in glass, or to **introduce new properties** such as "self-cleaning" effects. In this document this first type of nanocoating will be discussed under the umbrella term "responsive nanocoatings".

Another important area of application of nanocoatings is **tribological coatings**. Tribology is the science and technology of interacting surfaces in relative motion. Tribological properties include friction,

lubrication and wear. Tribological coatings are those coatings that are applied to the surface of a component in order to control its friction and wear. In this area the term "thin films" is often employed as an alternative to nanocoatings due to the fact that it is an area of innovation that started years ago and has now reached the nanoscale.

Tribological nanocoatings

Tribological coatings play a key role in the performance of internal mechanical components of a vehicle, such as the engine and powertrain. They are also key elements in **cutting tools and machinery in general**. By reducing wear and friction these coatings increase the lifetime of the working material while also reducing the dissipation of energy as heat, thus increasing the efficiency of the moving part. When applied to machinery and tools, tribological coatings can reduce (or eliminate) the need for lubricants, increase cutting speed, increase the rate of material removal, reduce maintenance costs or reduce processing cycle times.

Traditional materials used in coatings for tribological applications are carbides, cemented carbides, metal ceramic oxides, nitrides and carbon-based coatings. Since the microstructure controls many of the physical properties of the coating, having a nano-scaled microstructure may lead to significant improvements in the coatings´ mechanical properties (e.g. hardness), chemical properties (e.g. corrosion resistance) and electrical properties. Thus nanocomposite coatings are now being investigated as alternatives to the traditional approach of using specific alloying elements in single-phase coating materials to improve, for instance, properties such as hardness. One type of **nanocomposite coatings** is multilayered thin-films made of different layers in the order of nanometres. These films are mostly used for their **enhanced hardness** and elastic moduli, which is higher in multilayered films than in homogeneous thin films of either component, and for their wear properties. Commercial multilayer coatings made with multilayer periods in the nanoscale range already exist, such as WC/C coatings used in the cutting tool industry. Other examples are films of alternating layers of TiN and NbN, or TiAlN/CrN multilayers, which are more efficient than TiAlN films.

Responsive nanocoatings

Responsive nanocoatings are those where the properties of the material in the coating **react to environmental conditions**, such as light or heat, either in a passive or an active way. These coatings allow changing the properties of some materials, such as glass, by conferring new or improved properties.

The use of glass is very common in modern buildings, since it allows the construction of transparent and seemingly lightweight structures. However the relative high transmittance of visible and infrared (IR) light is a major disadvantage, since this leads to a large heat transfer which is particularly undesirable in summer. The problem is reversed in winter, when heat is dispersed through the glass. In order to address these problems various types of **nano-coatings that modulate light transmission in glass** are under investigation and being commercialised. The aim is to reduce indoor heating in summer, so less air-conditioning is required to keep the atmosphere cool, with consequent energy saving. One type of coating, referred to as "low-e" meaning "low emissivity", is based on a thin silver film, about 10nm thick, surrounded by dielectric layers. Metallic layers have been widely used to increase the reflectivity of light (and reduce transmittance) for years, but they have the disadvantage of giving a mirror-like appearance. Silver loses its metallic appearance when scaled to a nano-film, thus eliminating this problem. Such a coating is commercialised by Von Ardenne.

"Low-e" coatings are a type of passive nano-coatings, since the properties of the layers are unperturbed during its operation. Another class of coatings used in glasses are those often described as dynamic or "**smart coatings**". In this case the environmental conditions, such as radiation intensity or temperature, induce a change in the properties of the coating (e.g. darkening of windows). When the effect is a change in the colour (meaning also transparency) they are called "**chromogenic smart materials**". The change can be induced actively, by pressing a button. This is the case of **electrochromic coatings** where applying a small voltage induces a change in transmittance, and in the case of **gaschromic coatings**, which change their transmittance in the presence of specific gases. Gaschromic glazing makes use of the properties of tungsten oxide thin films (WO_3) which go from colourless to blue in the presence of hydrogen with a suitable catalyst. Gaschromic windows follow a double pane model: on one pane a film of WO_3 is deposited with a thin layer of catalysts on top. Hydrogen gas is fed into the gap producing colouration (windows colour with 1.1-10 % hydrogen, which is below the flammability concentration). To switch the colour of the window back, another gas is purged in (oxygen). Smart coatings can also be passive in the sense of changing their optical properties due to a change of external temperature (**thermochromic)** or light incidence (**photochromic**). Another example of nanotechnology applied to smart coatings is the use of a family of wavelength-selective films for manufacturing "heat mirrors". One of these materials is indium-tin-oxide (ITO), an infrared absorber. A 300 nm ITO coating on glass provides more than 80% transmission for the wavelengths predominant in sunlight. The transmission properties of the window can be varied by changing the thickness and material

composition of the coating, so that a combination of materials could be used to produce smart windows that reflect solar energy in summer but transmit solar energy in winter.

Self-cleaning surfaces

Another example of functional nanocoating is **photocatalytic coatings** (commercialised as "self-cleaning" glass) which use the catalytic properties of titanium dioxide (TiO_2). Pilkington Activ™ Self Cleaning Glass is a commercial example of a glass with a photocatalytic coating that renders the material easier to clean. **Superhydrophobic coatings** have surfaces that mimic the surface found in the lotus leaf (see **Chapter 2 "Natural Nanomaterials"** for details) and are being developed for many applications that require resistance to dirt and ease of cleaning. Both materials are covered in **Chapter 2 of Module 2 "Application of nanotechnologies: Environment"**.