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Polymer Nanocomposites

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Summary

The combination of good mechanical and chemical properties in polymers with the low density and low cost, made them to be a good candidate for making components in everyday life. The performances of polymers have been further improved by addition of nanoparticles. Polymers containing nanofillers have received considerable attention, due to their novel mechanical and electrical properties which can be used in several applications. The nanocomposite differs from microcomposite due to the high surface area to volume ratio of the nanofillers in comparison to microfillers. This allows achieving more enhancements in the properties of the polymer at much smaller filler concentration. The nanofillers can be made from spherical particles (such as metal nanoparticles), plate like structures (such as clay) or fiber like structures (such as carbon nanotubes). The properties of the nanocomposite are mainly dependent on the type of the filler, type of the polymer and the methodology used to prepare the nanocomposite. Thus, addition of each type of these fillers results in various changes in the properties of the polymers.

Depending on which of the properties of the polymer is improved, the resulting polymer nanocomposites can be applied for various applications. These are including components for electrostatic charge dissipation, electromagnetic shielding, microwave absorption, automobiles, actuators, and sensors.

The aim of this report is to provide a background information on polymers, type of the nanofillers used in the polymers. In addition, to review the potential of polymer nanocomposite for application in electronics, automobile and defence industry.

Chapter 1

Introduction

Nanoparticles of gold and silver have been found in Ming dynasty pottery and stained glass windows in medieval churches. However, the origins of nanotechnology did not occur until 1959, when Richard Feynman, US physicist and Nobel Prize winner, presented a talk to the American Physical Society annual meeting entitled "There is Plenty of Room at the Bottom". In his talk, Feynman presented ideas for creating nanoscale machines to manipulate, control and image matter at the atomic scale. In 1974, Norio Taniguchi introduced the term "nanotechnology" to represent extra-high precision and ultra-fine dimensions, and also predicted improvements in integrated circuits, optoelectronic devices, mechanical devices and computer memory devices. This is the so called "top-down approach" of carving small things from large structures. In 1986, K. Eric Drexler in his book *Engines of Creation* discussed the future of nanotechnology, particularly the creation of larger objects from their atomic and molecular components, the so called "bottom-up approach". He proposed ideas for "molecular nanotechnology" which is the self assembly of molecules into an ordered and functional structure [12].

The invention of the scanning tunneling microscope by Gerd Binnig and Heinrich Rohrer in 1981 (IBM Zurich Laboratories), provided the real breakthrough and the opportunity to manipulate and image structures at the nanoscale. Subsequently, the atomic force microscope was invented in 1986, allowing imaging of structures at the atomic scale. Another major breakthrough in the field of nanotechnology occurred in 1985 when Harry Kroto, Robert Curl and Richard Smalley invented a new form of carbon called fullerenes (buckyballs), a single molecule of 60 carbon atoms arranged in the shape of a soccer ball. This led to a Nobel Prize in Chemistry in 1996 [12]. The term nanotechnology comes from the combination of two words: the Greek numerical prefix nano referring to a billionth and the word technology. As an outcome, Nanotechnology or Nanoscaled Technology is generally considered to be at a size below $1 \mu m$ or $100 nm$ (a nanometer is one billionth of a meter, 10^{-9} m). Nanoscale science (or nanoscience) studies the phenomena, properties, and responses of materials at atomic, molecular, and macromolecular scales, and in general

at sizes between 1 and 100 *nm*. In this scale, and especially below 5 *nm*, the properties of matter differ significantly (i.e., quantum-scale effects play an important role) from that at a larger particulate scale. Nanotechnology is then the design, the manipulation, the building, the production and application, by controlling the shape and size, the properties-responses and functionality of structures, and devices and systems of the order or less than 100 *nm*. Nanotechnology is considered an emerging technology due to the possibility to advance well-established products and to create new products with totally new characteristics and functions with enormous potential in a wide range of applications. In addition to various industrial uses, great innovations are foreseen in information and communication technology, in biology and biotechnology, in medicine and medical technology, in metrology, etc. Significant applications of nanosciences and nanoengineering lie in the fields of pharmaceuticals, cosmetics, processed food, chemical engineering, high-performance materials, electronics, precision mechanics, optics, energy production, and environmental sciences [13]. The field of nanotechnology is one of the most popular areas for current research and development in basically all technical disciplines. This obviously includes polymer science and technology and even in this field the investigations cover a broad range of topics. This would include microelectronics (which could now be referred to as nanoelectronics) as the critical dimension scale for modern devices is now below 100 *nm*. Other areas include polymer-based biomaterials, nanoparticle drug delivery, miniemulsion particles, fuel cell electrode polymer bound catalysts, layer-by-layer self-assembled polymer films, electrospun nanofibers, imprint lithography, polymer blends and nanocomposites. Even in the field of nanocomposites, many diverse topics exist including composite reinforcement, barrier properties, flame resistance, electro-optical properties, cosmetic applications, bactericidal properties. Nanotechnology is not new to polymer science as prior studies before the age of nanotechnology involved nanoscale dimensions but were not specifically referred to as nanotechnology until recently. Phase separated polymer blends often achieve nanoscale phase dimensions; block copolymer domain morphology is usually at the nanoscale level; asymmetric membranes often have nanoscale void structure, miniemulsion particles are below 100 *nm*; and interfacial phenomena in blends and composites involve nanoscale dimensions. Even with nanocomposites, carbon black reinforcement of elastomers, colloidal silica modification and even naturally occurring fiber (e.g., asbestos-nanoscale fiber diameter) reinforcement are subjects that have been investigated for decades. In essence, the nanoscale of dimensions is the transition zone between the macrolevel and the molecular level [2]. In the last 20 years, there has been a strong emphasis on the development of polymeric nanocomposites, where at least one of the dimensions of the filler material is of the order of a nanometer. The final product does not have to be in nanoscale, but can be micro- or macroscopic in size [1].

A new way and perspective on improving properties of polymeric materials in order to make them more suitable for applications is the incorporation of nanoparticles. An inter-

esting type of fillers to be used as reinforcement in polymeric materials are carbon based nanomaterials, metallic nanoparticles and ceramic nanoparticles. Fillers are typically used to enhance specific properties of polymers and the polymer/nanocomposites based on nanomaterials have gained attention due to their ability to improve mechanical, thermal, barrier, fire retardant properties and electrical of polymers. Polymer/nanocomposites have been shown at lower or equal loadings to have properties that are equal or better than those of polymer composites with conventional filler [1].

The aim of this report is to review the properties of polymer nanocomposites and highlight their potential application in the automobile, electronics, and medical industry.

Chapter 2

Introduction to polymer

2.1 Introduction

In this chapter the basic background on polymers, their classification of thermal and mechanical properties are covered in this chapter.

2.2 Classification of polymer

The word polymer is derived from classical Greek poly meaning "many" and meres meaning "parts" or "molecule" Thus a polymer is a large molecule (macromolecule) built up by the repetition of small chemical units [3]. Polymers can be classified in many different ways. The most obvious classification is based on the origin of the polymer, i.e., natural vs. synthetic. Other classifications are based on the polymer structure, polymerization mechanism, preparative techniques, or thermal behavior [4].

2.2.1 Molecular structure

Polymer is formed when a very large number of structural units (repeating units, monomers) are made to link up by covalent bonds under appropriate conditions. Certainly even if the conditions are "right" not all simple (small) organic molecules possess the ability to form polymers. In order to understand the type of molecules that can form a polymer, let us introduce the term functionality. The functionality of a molecule is simply its interlinking capacity, or the number of sites it has available for bonding with other molecules under the specific polymerization conditions. These structures can be classified into four different categories: (i) linear, (ii) branched, (iii) crosslinked, and (iv) network. In linear polymers, the mers are joined together end to end in single chains (see Figure 2.1 a). The long chains are flexible and may be considered as a mass of spaghetti. Extensive van der Waals bonding between the chains exist in these polymers. Some of the common linear polymers are

polyethylene, polyvinyl chloride, polystyrene, nylon and the fluorocarbons. Polymers may also have a molecular structure in which side-branch chains are connected to the main ones, as shown schematically in Figure 2.1 b. These polymers are called branched polymers. The branches result from side reactions that occur during the synthesis of the polymer. The formation of side branches reduces the chain packing efficiency, resulting in a lowering of the polymer density. In crosslinked polymers, adjacent linear chains are joined to one and another at various positions along their lengths as depicted in Figure 2.1 c. Generally, crosslinking is accomplished by additive atoms or molecules that are covalently bonded to the chains. Many of the rubber materials consist of polybutadiene crosslinked with S atoms. Trifunctional mer units, having three active covalent bonds, form three-dimensional networks as shown in Figure 2.1 d. Polymers consisting of trifunctional units are termed network polymers.

The molecular structure of a polymer has significant effects on its mechanical and thermal properties. In general, as the strength of the connections between the chains increases, the thermal and mechanical stability of the material increases. These connections might be intermolecular bonds (van der Waals, dipolar, or H bonds) or covalent crosslinks. [4].

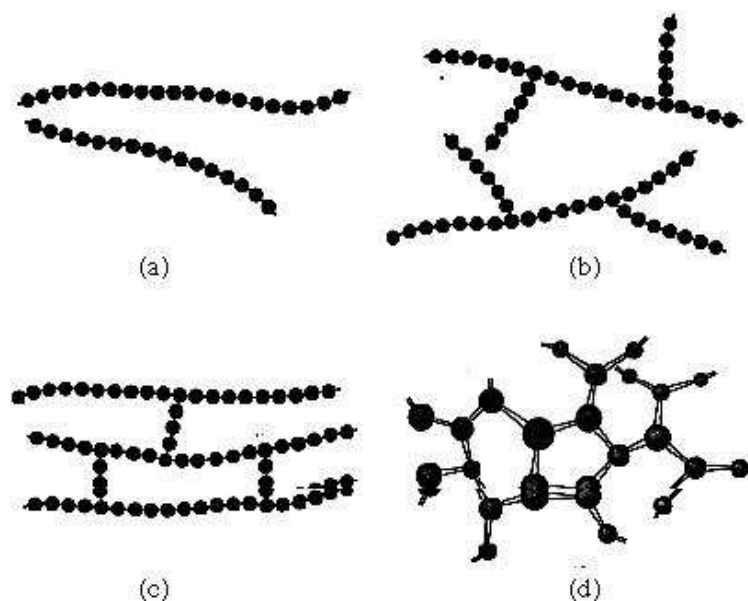


Figure 2.1: Schematic illustrations of (a) linear, (b) branched, (c) crosslinked, and (d) network (three-dimensional) molecular structures.

2.2.2 Natural VS. Synthetic

Polymers may either be naturally occurring or purely synthetic. All the conversion processes occurring in our body (e.g., generation of energy from our food intake) are due to the presence of enzymes. Life itself may cease if there is a deficiency of these enzymes. Enzymes, nucleic acids, and proteins are polymers of biological origin. Their structures, which are normally very complex, were not understood until very recently. Starch a staple food in most cultures cellulose, and natural rubber, on the other hand, are examples of polymers of plant origin and have relatively simpler structures than those of enzymes or proteins. There are a large number of synthetic (man-made) polymers consisting of various families: fibers, elastomers, plastics, adhesives, etc. Each family itself has subgroups [3].

2.2.3 Amorphous or Crystalline

Structurally, polymers in the solid state may be amorphous "non-crystalline solid" or crystalline. When polymers are cooled the molten state or concentrated from the solution, molecules are often attracted to each other and tend to aggregate as closely as possible into a solid with the least possible potential energy. For some polymers, in the process of forming a solid, individual chains are folded and packed regularly in an orderly fashion. The resulting solid is a crystalline polymer with a long-range, three-dimensional, ordered arrangement. However, since the polymer chains are very long, it is impossible for the chains to fit into a perfect arrangement equivalent to that observed in low-molecular-weight materials. A measure of imperfection always exists. The degree of crystallinity, i.e., the fraction of the total polymer in the crystalline regions, may vary from a few percentage points to about 90 percent depending on the crystallization conditions [3].

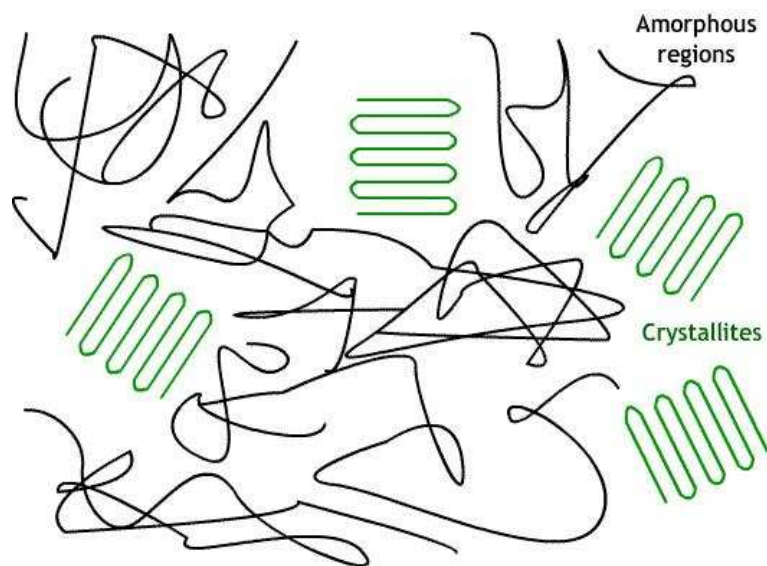


Figure 2.2: Amorphous and Crystalline

2.2.4 Homopolymers or Copolymer

Polymers may be either homopolymers or copolymers depending on the composition. Polymers composed of only one repeating unit in the polymer molecules are known as homopolymers. However, chemists have developed techniques to build polymer chains containing more than one repeating unit. Polymers composed of two different repeating units in the polymer molecule are defined as copolymers [3].

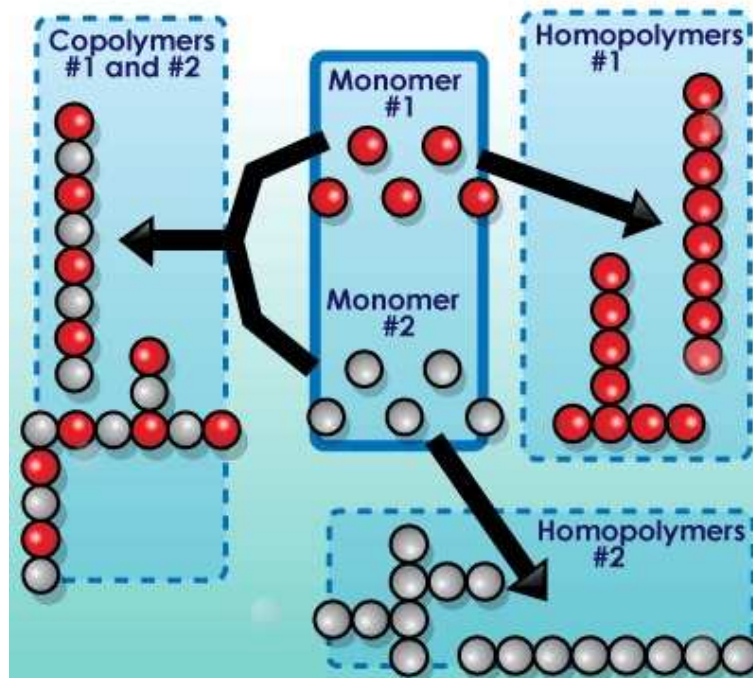


Figure 2.3: Homopolymers and Copolymer

2.2.5 Thermoplastics Vs Thermosets

The name thermoplastic is given to polymeric materials that are flexible at high temperatures. Usually they are simply referred to as plastics. For example, a polyethylene milk jug can be dented without much force. Polymers such as polyethylene can form either fibers or thermoplastics, depending on how they are processed. A thermoplastic sample has chains going in random directions, held together by weak secondary bonds. A small amount of force can make the chains slide around, thus changing the shape of the sample [6].

With certain polymers, heat can cause crosslinks to form irreversibly. The sample hardens so its shape is "set." Epoxy resins and some polycarbonates belong in this category. Unlike thermoplastics, thermoset samples will not soften upon heating [6].

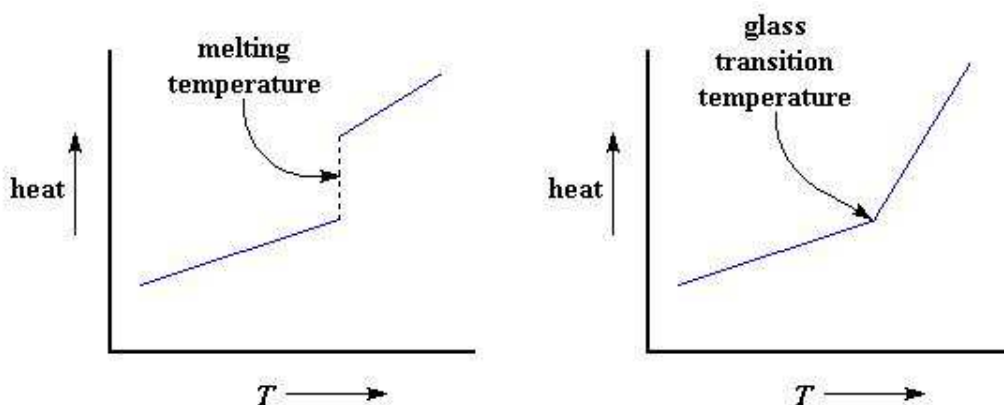
2.3 Properties of polymers

2.3.1 Thermal properties

The thermal behavior of polymers is of considerable technological importance. At elevated temperatures, the behavior of polymers is much more complex because thermally activated rearrangements and movements within and between the chains can occur, which are frequently reversible. These processes are mainly responsible for the physical and mechanical properties of polymers. Knowledge of thermal transitions is important in the selection of proper processing and fabrication conditions, the characterization of the physical and mechanical properties of a material, and hence the determination of appropriate end uses [3].

i- Glass transition and Melting temperature

If a polymer is amorphous, the solid-to-liquid transition occurs very gradually, going through an intermediate, rubbery state without a phase transformation. The transition from the hard and brittle glass into a softer, rubbery state occurs over a narrow temperature range referred to as the glass transition temperature. In the case of a partially crystalline polymer, the above transformation occurs only in the amorphous regions. The crystalline zones remain unchanged and act as reinforcing elements thus making the sample hard and tough. If heating is continued, a temperature is reached at which the crystalline zones begin to melt. The equilibrium crystalline melting point, T_m , for polymers corresponds to the temperature at which the last crystallite starts melting. Again, in contrast to simple materials, the value of T_m depends on the degree of crystallinity and size distribution of crystallites. The general changes in physical state due to changes in temperature and molecular weight are shown in Figure 2.3.1 for amorphous and crystalline polymers [3].



A heat vs. temperature plot for an crystalline polymer, on the left; and a amorphous polymer on the right.

ii- Viscous behavior and viscoelasticity

Fluids show a characteristic resistance to movement (flow), which is called viscosity. Viscosity results in a frictional energy loss, which dissipates in the fluid as heat. Polymeric materials behave both as viscous fluids and elastic solids. They are viscoelastic materials. The most important characteristic of viscoelastic materials is that their mechanical properties depend on time. Viscosity is a measure of the friction and the associated energy dissipation between molecules of fluids. Polymeric materials due to their macromolecular (long-chain) structure are expected to have high viscosities [5].

2.3.2 mechanical properties of polymers

The elastic behavior of polymers is mainly determined by the intermolecular bonds between the chain molecules, not by the covalent bonds within. For elastomer and duromers (is a supplier of high-performance plastic compounds), the covalent bonds linking the chains are also relevant. In the following, we will start by discussing the elastic properties of thermoplastics and afterwards study the influence of cross-linking.

Whenever a force is exerted on a solid material, the material will deform in response to the force. Depending on the particular orientation of the force with respect to the material surface different types of forces can be identified. In Figure 2.4, some common types of forces are depicted. A mechanical test using tensile forces is called a tensile test. The compressive strength is the capacity of a material or structure to withstand loads tending to reduce size. Shearing forces are unaligned forces pushing one part of a body in one direction, and another part the body in the opposite direction. When the forces are aligned into each other, they are called compression forces [5]. A material inelastic, if upon an applied force, its

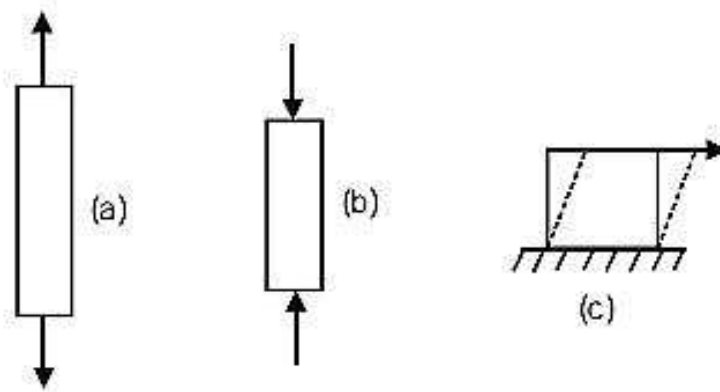


Figure 2.4: Examples of types of forces: (a) Tensile force. (b) Compressive force. (c) Shear force.

deformation is instantaneous and constant, and upon the removal of the force, its recovery is instantaneous and complete (i.e. the material will return to its original shape).

In order to make the analysis of a mechanical test independent of the materials size, it is useful to define a quantity called stress; It is defined as the force F divided by the cross-sectional area A of the material [units $N/m^2 = Pa$]. The deformation is quantified by the strain ε which is defined as the length change Δl divided by the initial length l_0 and it is dimensionless. In case of a tensile test the strain is often called elongation and is usually expressed as a percentage increase in length compared to the initial length [5].

The stress-strain relationship is given by the following equation

$$\sigma = E\varepsilon \quad (2.1)$$

i- Stress-strain behavior in polymer

If a material is subjected to high-strain deformation, it deforms permanently (plastic deformation) and ultimately fails. In Figure 2.5, we show a graph of stress-strain behavior over the entire strain range and the ultimate failure (rupture) for a typical polymeric material subjected to a tensile test. For sufficiently low stresses and strains, the polymeric material behaves as a linear elastic solid. The point where the behavior starts to be non-linear is called the proportional limit. The local maximum in the stress-strain curve is called the yield point and indicates the onset of plastic (i.e. permanent) deformation. The corresponding stress and elongation are called yield strength and elongation at yield. Beyond the yield point the material stretches out considerably and a "neck" is formed; this region is called the plastic region. Further elongation leads to an abrupt increase in stress (strain hardening) and the ultimate up turn of the material. At the rupture point the corresponding stress and strain are called the ultimate strength and the elongation at break, respectively.

The stress-strain behavior of a polymeric material depends on various parameters such as molecular characteristics, micro-structure, strain-rate and temperature. [5]. The observed

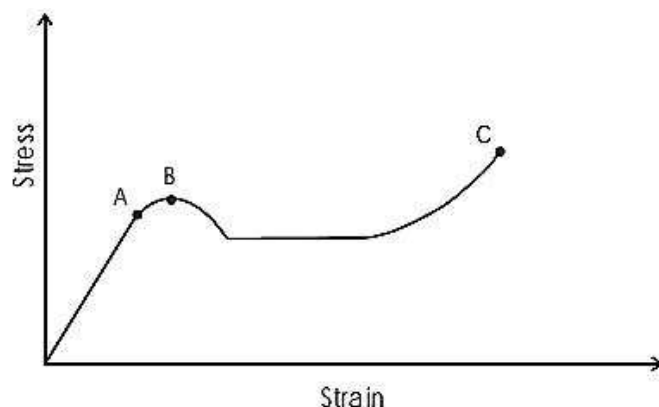


Figure 2.5: Typical stress-strain curve of a polymeric material. A is the proportional point, B the yield point and C the rupture (break) point.

elastic behavior of solids at low stress-strains is due to the stretching of their chemical bonds, which are inherently short-range. Particularly in polymers, although the above mechanism cannot be excluded, the elastic behavior is more complicated due to the chain-like structure of the macromolecules [5].

ii- Creep

The deformation of a material over time due to the application of a constant load is called creep Figure 2.6. A purely elastic material responds instantaneously to the load and the deformation remains the same, in addition, it will recover its initial shape upon the removal of the load. On the contrary, a viscous liquid will deform as long as the load continues to be applied. Upon the removal of the load, the fluid does not return to its initial position. The response of a viscoelastic material is intermediate between the solid and the liquid (see Figure 2.6 d). Creep depends on the applied load, molecular characteristics, micro-structure and temperature. Creep, flow and plastic deformation in polymeric materials results from the irreversible slippage, decoupling and disentanglements of polymer chains (or groups of chains in semi-crystalline polymers) [5].

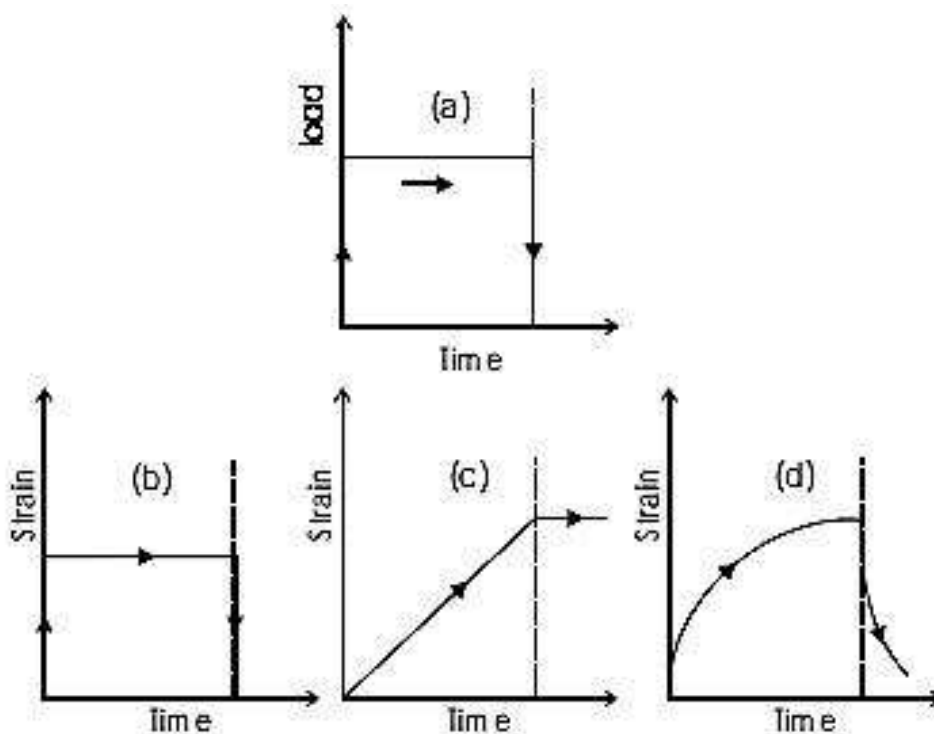


Figure 2.6: Mechanical response (deformation) of a material subjected to a constant load for a finite time interval (up to the dotted line). (a) Load application; (b) solid, elastic behavior (c) liquid, viscous flow behaviour (d) polymer, viscoelastic behavior.

Chapter 3

Nanocomposites

3.1 Introduction

This chapter provide an over view about nanomaterials, their properties and applications. Following introduction a brief discussion on the classification and properties of nanomaterials are presented. The properties of nanomaterials that distinguish them from materials are discussed. Finally, the application of nanomaterials are covered.

3.2 Nanomaterials

Nanomaterials are materials that have structural components smaller than 1 nm in at least one dimension. While the atomic and molecular building blocks (0.2 nm) of matter are considered nanomaterials, examples such as bulk crystals with lattice spacing of nanometers but macroscopic dimensions overall, are commonly excluded [8].

The transition from microparticles to nanoparticles yields dramatic changes in physical properties. Nanoscale materials have a large surface area for a given volume. Since many important chemical and physical interactions are governed by surfaces and surface properties, a nanostructured material can have substantially different properties from a larger-dimensional material of the same composition. In the case of particles and fibers, the surface area per unit volume is inversely proportional to the material's diameter, thus, the smaller the diameter, the greater the surface area per unit volume, in Figure 3.1 [1]. Surface area to volume ratio; Nanomaterials have a relatively larger surface area when compared to the same volume or mass of the material produced in a larger form. When the given volume is divided into smaller pieces the surface area increases. So the particle size decreases a greater proportion of atoms are found at the surface compared to those inside. Hence Nanoparticles have a much greater surface area per given volume compared with larger particles. It makes materials more chemically reactive.

Two principal factors cause the properties of nanomaterials to differ significantly from other materials: increased relative surface area and quantum effects [7].

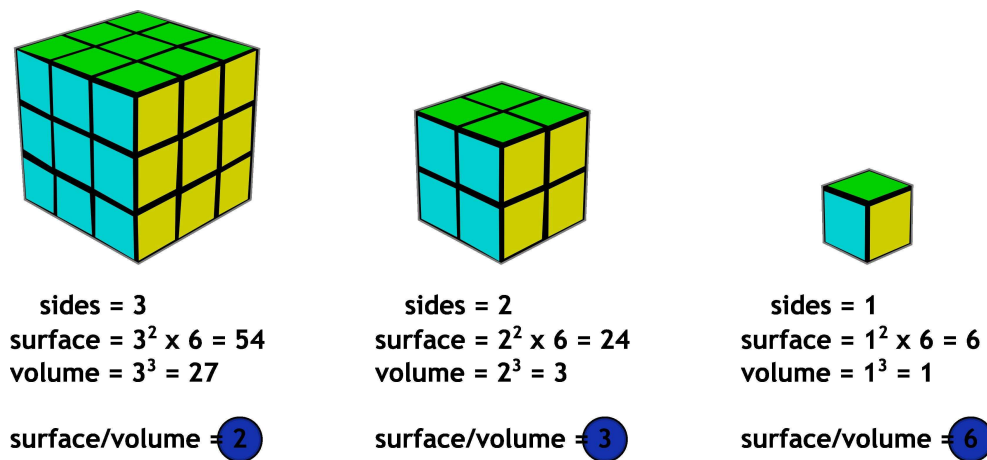


Figure 3.1: The surface area per unit volume

3.2.1 Classification

Nanomaterials have extremely small size which having at least one dimension 100 *nm* or less[16]. As shape, or morphology, of nanoparticles plays an important role in their properties, it is useful to classify them based on their number of dimensions (D) Figure3.2 [8]. Nanoparticles are generally classified based on their dimensionality in this way:

i- Zero Dimension (0D) nanomaterials

These nanostructures possess nano-dimensions in all the three directions. These includes nanoparticles [e.g. gold, silver nanoparticles etc], quantum dots. Many of these are spherical and the diameter of these particles will be in the 1-50 *nm* range. These can have different shapes such as cubes.

ii- one Dimension (1D) nanomaterials

In these nanostructures, one dimension of the nanostructure will be outside the nanometer range. These include nanowires, nanorods, and nanotubes. These materials are long (several micrometer in length), but with diameter of only a few nanometer. Nanowire and nanotubes of metals, oxides and other materials have been made.

iii- two Dimension (2D) nanomaterials

In this type of nanomaterials, two dimensions are outside the nanometer range. These include nano films (e.g. coatings and thin-film-multilayers), nanosheets or nano walls. The area of the nano films can be large (several micrometer), but their thickness is very small (only few nanometers).

iv- three Dimension (3D) nanomaterials

In these, the three dimensions of the nanostructure are outside the nanometer range. These include bulk materials, Where the size of the individual blocks (or structural units) are in the nanometer scale (1-100 *nm*).

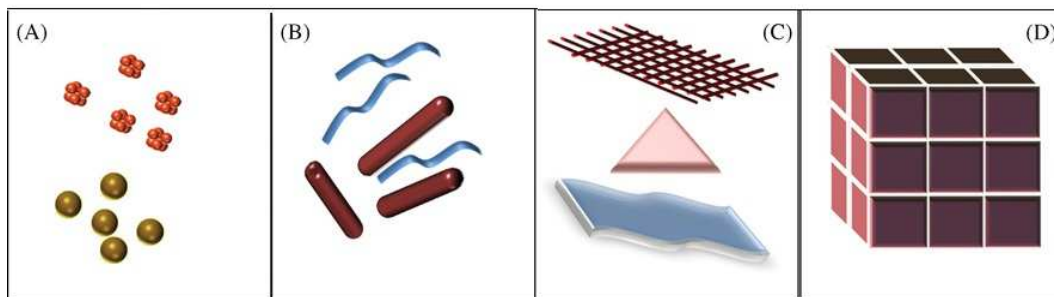


Figure 3.2: Classification of Nanomaterials (a) 0D spheres and clusters, (b) 1D nanofibers, wires, and rods, (c) 2D films, plates, and networks, (d) 3D nanomaterials.

3.2.2 Synthesis and processing

Nanomaterials deal with very fine structures: a nanometer is a billionth of a meter. This indeed allows us to think in both the 'bottom up' or the 'top down' approaches (Figure 3.3) to synthesize nanomaterials, i.e. either to assemble atoms together or to dis-assemble (break, or dissociate) bulk solids into finer pieces until they are constituted of only a few atoms. Nanomaterials are synthesis by two main approaches which are top down and bottom up approaches. In the bottom up method atoms are assemble together to form nanostructure. Whereas in top down approach the bulk solid material are braked into finer pieces in which have dimension in nanoscales.

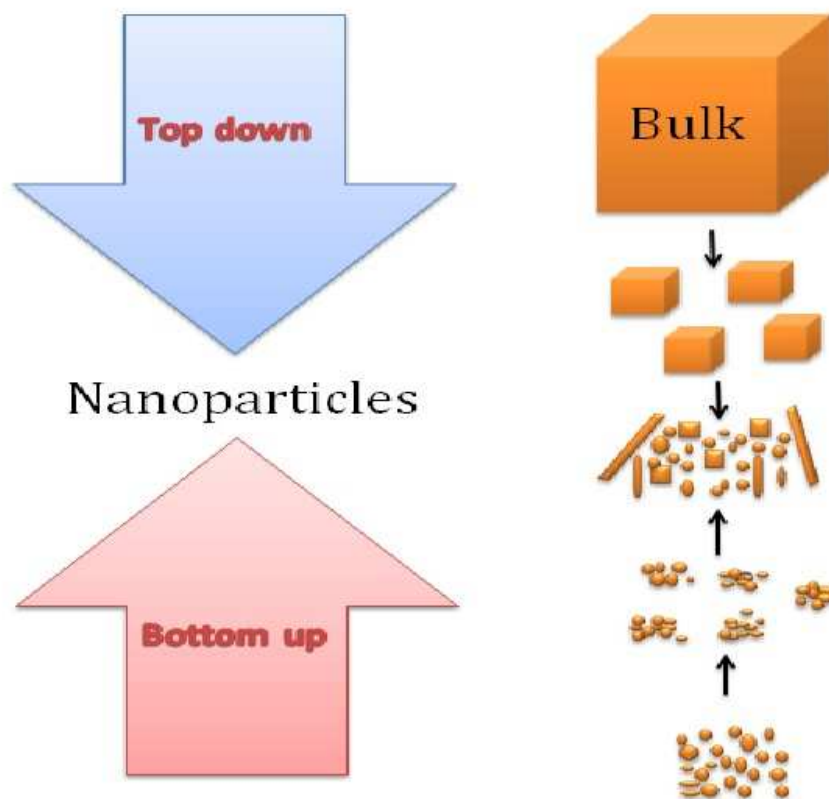


Figure 3.3: Bottom up and Top down

3.2.3 Properties of Nanomaterials

Between the dimensions on an atomic scale and the normal dimensions, which characterize bulk material is a size range where condensed matter exhibits some remarkable specific properties that may be significantly different from the physical properties of bulk materials. Some such peculiar properties are known, but there may be a lot more to be discovered. Some known physical properties of nanomaterials are related to different origins: for example, (i) large fraction of surface atoms, (ii) large surface energy, (iii) spatial confinement, and (iv) reduced imperfections.

The following are just a few examples:

1. Nanomaterials may have a significantly lower melting point or phase transition temperature and appreciably reduced lattice constants, due to a huge fraction of surface atoms in the total amount of atoms.
2. Mechanical properties of nanomaterials may reach the theoretical strength, which are one or two orders of magnitude higher than that of single crystals in the bulk form. The enhancement in mechanical strength is simply due to the reduced probability of defects.
3. Optical properties of nanomaterials can be significantly different from bulk crystals. For example, the optical absorption peak of a semiconductor nanoparticle shifts to a short wavelength, due to an increased band gap. The color of metallic nanoparticles may change with their sizes due to surface plasmon resonance.
4. Electrical conductivity decreases with a reduced dimension due to increased surface scattering. However, electrical conductivity of nanomaterials could also be enhanced appreciably, due to the better ordering in microstructure, e.g. in polymeric fibrils.
5. Magnetic properties of nanostructured materials are distinctly different from that of bulk materials. Ferromagnetism (is the basic mechanism by which certain materials (such as iron) form permanent magnets, or are attracted to magnets.) of bulk materials disappears and transfers to superparamagnetism(is a form of magnetism, which appears in small ferromagnetic or ferrimagnetic nanoparticles.) in the nanometer scale due to the huge surface energy [9].

3.3 Polymer nanocomposites

A nanocomposite material is a nano combination of two or more distinct materials (one of nano scale or both in nano scale), having a recognizable interface between them. Nanocomposites are used not only for their structural properties, but also for electrical, thermal, and environmental applications. Modern nanocomposite materials are usually optimized to achieve a particular balance of properties for a given range of applications [17]. The major composite classes include organic-matrix composites (OMCs), metal-matrix composites (MMCs), and ceramic-matrix composites (CMCs). The term "organic-matrix composite" is generally assumed to include two classes of composites: polymer-matrix composites (PMCs) and carbon-matrix composites [17].

Polymer nanocomposites can be defined as two-phase systems consisting of polymers and fillers of which at least one dimension is in the nano-range (1-100 *nm*). The nanofillers can be one-dimensional nanotubes or nanofibers, two-dimensional clay platelets, or three-dimensional spherical particles[1]. Scientists for improve the properties of composite materials investigate composites with lower and lower fillers size, leading to the development of microcomposites and the recent trend in composite research is nanocomposites. Nanocomposites refer to composites in which one phase has nano scale morphology such as nanoparticles, nanotubes or lamellar nanostructure. The improvement of the properties by the addition of particles can be achieved when:

1. Adequately good interaction between the nanoparticles and the matrix
2. Good dispersion of particles within the matrix.

In nanocomposites, covalent bonds, ionic bonds, Vander Waals forces, hydrogen bonding could exist between the matrix and filler components [19].

The advantage of nanoparticles is that, because of its high specific surface area, already at low concentrations major effects on the macroscopic properties can be obtained. Over the past years, polymer nanocomposites have attracted considerable interest in both academia and industry, but one of the outstanding problems is to control the state of dispersion of the nanoparticles, which is highly determined by the preparation method. Therefore, different preparation methods for polymer nanocomposites [1]. Some nanocomposites may show properties predominated by the interfacial interactions and others may exhibit the quantum effects associated with nanodimensional structures. Efficient nanoparticle dispersion combined with good polymer, particle inter facial adhesion eliminates scattering and allows the exciting possibility of developing strong yet transparent films, coatings and membranes [7].

Advantages of nanocomposite Materials, nanocomposites have many engineering advantages over synthetic polymers and copolymers. Some of these advantages are:

1. Reinforcement of the resin resulting in increased tensile strength, flexural strength, compression strength, impact strength, rigidity and combination of these properties.
2. Increased size stability.
3. Improved fire retardancy.
4. Corrosion protection.
5. Improved electrical properties; reduction of dielectric constant.
6. Coloring.
7. Improved processibility; controlled viscosities, good mixing, controlled orientation of fibers.

One of the most important properties of nanocomposite materials offer is the strength per density or modulus per density termed as specific strength and specific modulus, respectively [18].

Disadvantages, as the use of nanomaterials in society increases, it is reasonable to assume that their presence in environmental media will increase proportionately, with consequences for human and environmental exposure. Despite of several advantages and benefits of nanotechnology in the field of medicine and electronics, est. It has been reported that the direct exposure to nanomaterials can cause serious health problem to the human and the life forms on the earth [14]. The motion of free nanoparticles is not constrained, and they can easily be released into the environment leading to human exposure that may pose a serious health risk. In contrast are the many objects containing nanostructured elements that are firmly attached to a larger object, where the fixed nanoparticles should pose no health risk when properly handled.[8]

Due to their extremely small size and relatively large surface areas, nanomaterials may interact with the environment in ways that differ from more conventional materials. Potentially harmful effects of nanotechnology could result from the nature of the nanoparticles themselves and from products made with them [15].

3.3.1 Nanoparticles of the polymer composites

Nanoparticles exist in spherical, tube and whisker, and plate-like shapes and at least one of the three dimensions is required to be on a nanometric scale. Nanostructures of layered clays are further categorized as intercalated, where the polymer chains have penetrated between the clay layers in a well-ordered multilayer morphology, and exfoliated, where the clay layers have dispersed along the matrix and have no organized structure. Carbon nanotubes also exhibit two nanostructures, single-walled tube, and multi-walled carbon nanotube, which is composed of several tubes within each other. Nanoparticles, like the conventional filler particles, can be prepared by breaking up a large particle (nanoclays and other minerals) or by building them from bottom up (carbon nanotubes and metal oxides). Regardless of the preparation method, it is important to inhibit agglomeration of the nanoparticles and ensure good adhesion to the matrix [10].

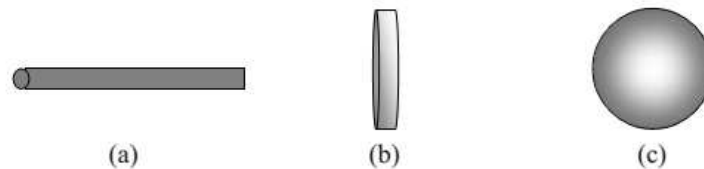


Figure 3.4: (a) Tube and Whisker, (b) Plate-like shapes, (c) Spherical

3.3.2 Classification of nanocomposites

Polymeric nanocomposites can be broadly classified as

1. Nanoclay-reinforced composites
2. Carbon nanotube-reinforced composites
3. Nanofibre-reinforced composites, and
4. Inorganic particle-reinforced composites.

i- Nanoclay-reinforced Composites

Historically, the term clay has been understood to be made of small inorganic particles (part of soil fraction $< 2\text{ mm}$), without any definite composition or crystallinity. The clay mineral (also called a phyllosilicate) is usually of a layered type and a fraction of hydrous, magnesium, or aluminum silicates [11].

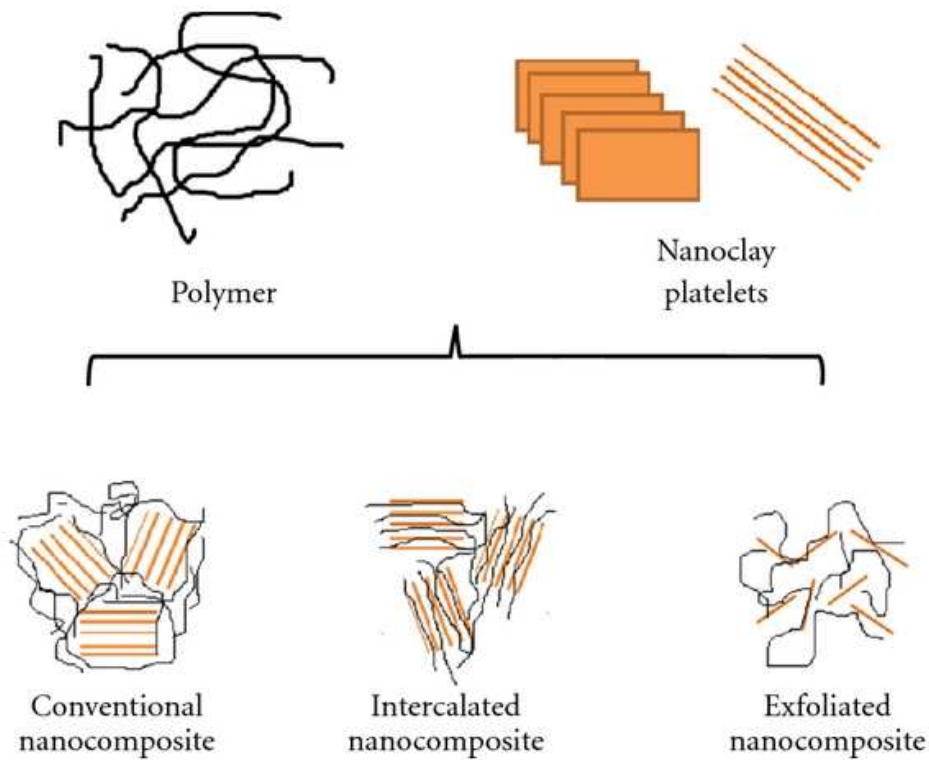


Figure 3.5: States of dispersion of nanoclay platelets.

ii- Carbon Nanotube-reinforced Composites

Micrometer-size carbon tubes, which are similar in structure (but not in dimensions) to the recently discovered multi-walled carbon nanotubes, were first found in 1960 by Roger Bacon. These nanosized, near-perfect whiskers (termed nanotubes) were first noticed and fully characterized in 1991 by Sumio Iijima of NEC Corporation in Japan [11].

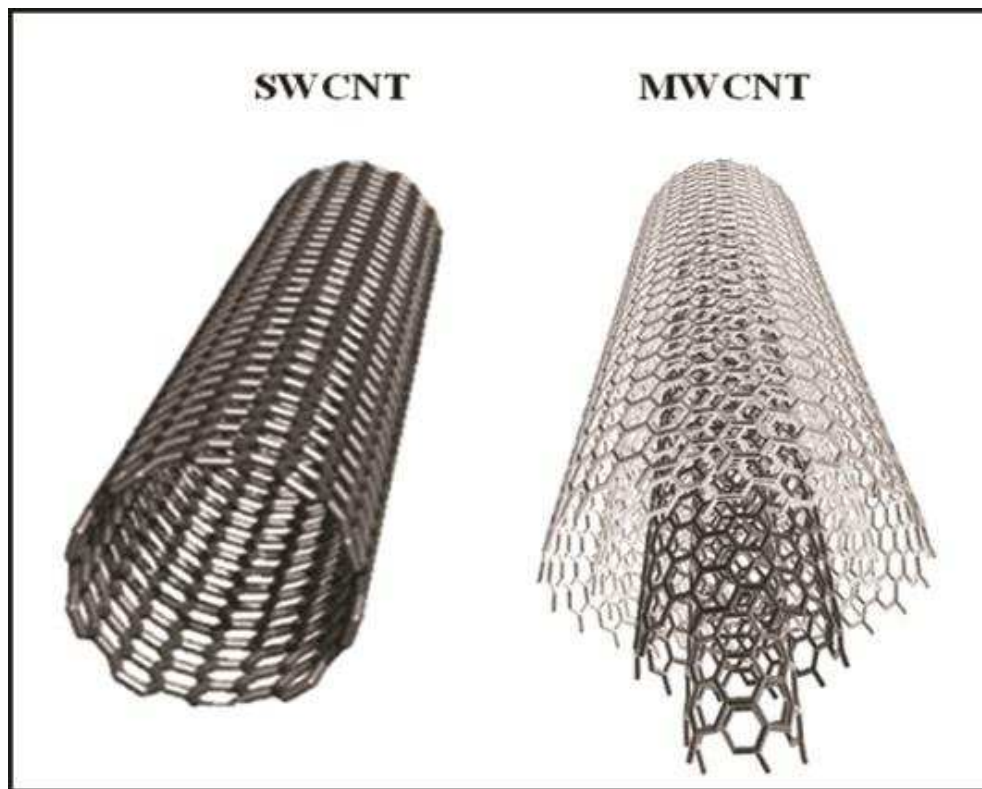


Figure 3.6: Carbon Nanotube: single-wall carbon nanotube (SWCNT), multi-wall carbon nanotube (MWCNT)

iii- Nanofiber-reinforced Composites

Carbon nanofibers (CNF) are a unique form of vapourgrown carbon fibers that fill the gap in physical properties between conventional carbon fibers (5-10 μm) and carbonnanotubes (1-10 nm). The reduced diameter of nanofiber provides a larger surface area with surface functionalities in the fiber. Typically CNF are not concentric cylinders; the length of the fiber can be varied from about 100 μm to several cm, and the diameter is of the order of 100-200 nm with an average aspect ratio greater than 100. The most common structure of CNF is the truncated cones, but there are wide ranges of morphologies (cone, stacked coins, etc) [11].



Figure 3.7: Fibers

iv- Inorganic Particle-reinforced Composites

Nanoparticles are often defined as particles of $< 100 nm$ in diameter. Nanometer-sized particles have been made from different organic-inorganic particles and these impart improved properties to composite materials. Different particles have been used to prepare polymer/inorganic particle nanocomposites, including:

- Metals (Al, Fe, Au, Ag, etc.).
- Metal oxides (ZnO, Al, CaCO₃, TiO₂, etc.).
- Nonmetal oxide (SiO₂).
- Other (SiC).

The selection of nanoparticles depends on the desired thermal, mechanical, and electrical properties of the nanocomposites [11].

3.3.3 Preparation of Polymer Nanocomposites

Polymeric nanocomposites have been intensely investigated due to the performance improvement achieved when a small amount of nanosized particles are added to a polymer matrix. The remarkable changes on physical and mechanical properties of polymers due to the addition of inorganic solid nanoparticles (typically in form of fibers, flakes, spheres or fine particles) is explained by the huge surface area, which increases the interaction between the nanoparticle and the polymer. There are three main methods have been used for fabricating polymer nanocomposites. These include melt mixing, solution and in-situ polymerisation methods. Each of these methods is compatible with particular types of polymer. Melt mixing is suitable for thermoplastic polymers which soften when heated. The solution mixing method is limited to those polymers which are able to dissolve in common solvents. In-situ polymerisation is mostly used to fabricate polymer-grafted filler with corresponding polymer-composite materials. This method is preferred for the preparation of insoluble and thermally unstable polymers which cannot be prepared by solution or melt processing.

Chapter 4

Application of polymer Nanocomposites

4.1 Introduction

Advantages of nanocomposite films are numerous and the possibilities for application in the packaging industry are endless. Because of the nanocomposite process's dispersion patterns, the platelets result in largely improved performance in the following properties:

- Gas, oxygen, water, etc. barrier properties
- High mechanical strength
- Thermal stability
- Chemical Stability
- Recyclability
- Dimensional stability
- Heat resistance
- Good optical clarity (since particles are nano-size).

This chapter covers the applications of polymer nanocomposites in fields of mechanical, electrical, optical applications.

4.2 High Performance Fiber/Fabrics

The first attempt to produce nanotubes resulted in very small quantities of tangled nanotubes, which however has created interest in these materials as non-oriented mats. Further developments had led to the development of techniques for spinning nanotubes into fibers in a polymer matrix, which is of special interest for mechanical and electronic fabric applications. By infiltrating nanotube mats or woven fibers with a polymer, continuous sheets or films of a nanocomposite can be produced. The nanotubes will contribute to mechanical properties (strength and stiffness) of the film as well as to electrical conductivity.

The production of polymer fibers was until recently limited to extruding fibers of relatively large (micrometer diameter) sizes. Recently, an electrospinning technique has been shown to be effective to produce pure polymer and polymer nanocomposite fibers with diameters in the range of 200 nm to 300 nm. More interesting is, in electrospun nanocomposite fibers, the nanoparticles were found to be highly aligned. This is likely to significantly effect the optical and mechanical properties, although no results were reported [11]. In many optical applications such as telecommunications and optical computing, polymer optical fibers are very attractive to adjust the refractive index of the connecting optical fiber (due to ease of mass production and low cost). This can be done by the addition of nanoparticles with various refractive indices to the polymer [11].

4.3 Microwave Absorbers

Nanocomposites as microwave absorbers are receiving much attention, synthesis of polypyrrole nanocomposites containing iron oxides, tin oxide, tungsten oxide and titanium dioxide have been investigated. Pyrrole containing a dispersion of nanoparticle metal oxides was polymerised in situ and the magnetic properties reported. The electrical conductivity and dielectric losses can be tuned by varying the concentration and orientation of the nanotubes additions. Have been awarded a patent in this area, covering a wide range of thermoplastic and thermosetting matrices containing oriented nanotubes. Only a few weight per cent of nanotubes need be added to the polymer to achieve useful properties. Efforts have been made to utilise carbon nanotubes CNTs for developing economical microwave (in the range 8 GHz to 24 GHz) absorbers. These materials have wide applications in electrical energy storage (condensers) integrated into load-carrying structures, high strength CNTs polymer fibers for energy absorption, electromagnetic shielding, etc [11].

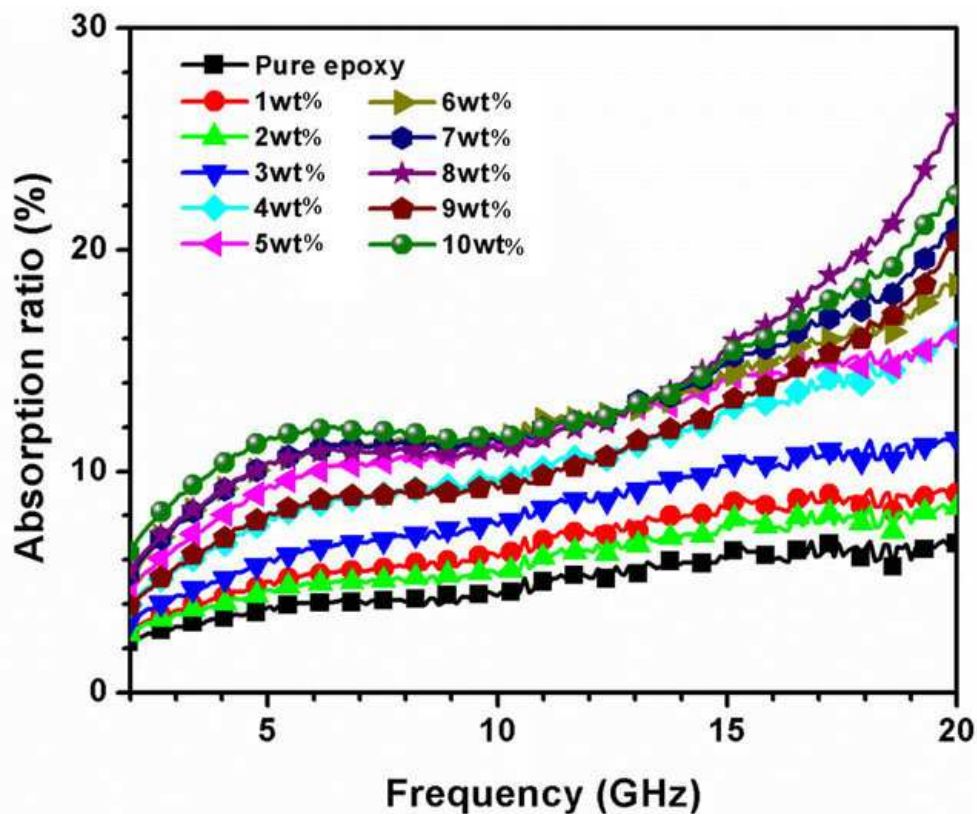


Figure 4.1: Absorption ratio of the MWCNTs-epoxy composite samples in the microwave frequency range from 2-20 GHz.

4.4 Electrostatic Charge Dissipation

Dissipation of static charge on spacecraft is a severe problem, which requires a material with not only sufficient electrical conductivity but also must be stable to the space environment (intense ultraviolet radiation, charged particle irradiation, atomic oxygen, rapid and severe temperature changes). The conductivity sufficient to eliminate static discharge could be achieved in a polyimide nanocomposite containing as little as 0.03 Wt per cent of CNTs. A method for manufacturing conductive composites. They first sonicated an organic polymer precursor (e.g., poly(arylene ether)) with single wall nanotubes SWNTs in an ultrasonicator to disperse the SWNTs and then polymerised the organic polymer precursor using shear and elongational forces. They claimed that in this way, at least a portion of the CNTs could be functionalised either at the side wall or hemispherical ends [11].

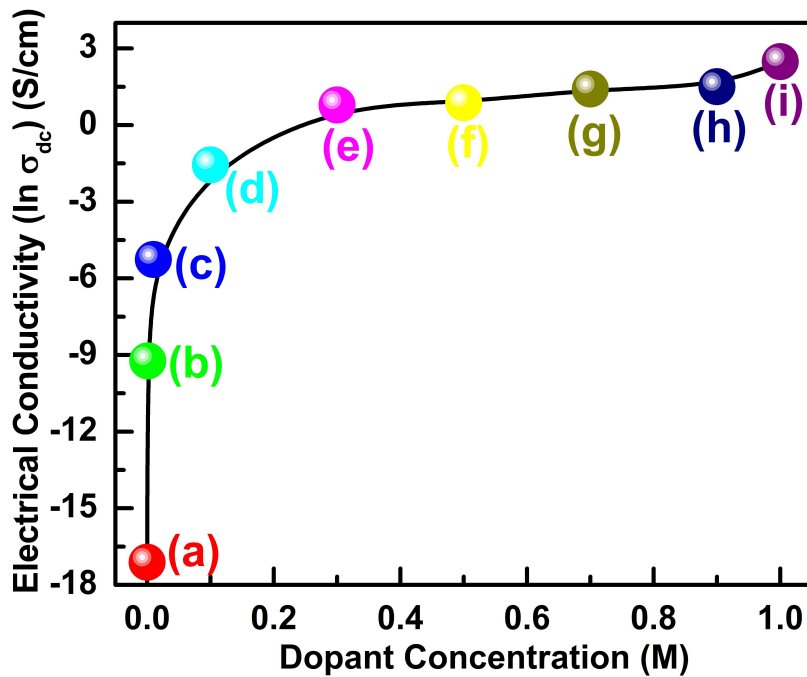


Figure 4.2: Variation of electrical conductivity of hydrochloric acid (HCl) doped Emeraldine base (EB) samples as a function of dopant (HCl) concentration (a) 0.0 M (b) 0.001 M, (c) 0.01 M, (d) 0.1 M, (e) 0.3 M, (f) 0.5 M, (g) 0.7 M, (h) 0.9 M and (i) 1.0 M.

4.5 Ultraviolet Irradiation Resistance

Common polymers are not stable under ultraviolet irradiation and will begin to degrade after few weeks. Strength and fracture toughness are drastically reduced and the polymer becomes brittle. The resistance to degradation by ultraviolet irradiation could be reduced by adding nanomaterials approximately half and mechanical properties could be improved by 80 per cent [11].

4.6 Fire Retardation

Polymers have poor fire resistance. If ignited, most polymers will burn quickly, releasing large quantities of heat, toxic gases, and soot. Polymers containing a few weight per cent of nanoparticle clays have greatly improved fire resistance. The thermal properties of the polymer nanocomposite PNC are improved, melting and dripping are delayed, and rate of burning is greatly reduced (by more than half). The presence of flake-like clay nanoparticles reduces the diffusion of polymer decomposition volatiles (the fuel) to the burning surface and reduces diffusion of air into the polymer. Further, addition of clay nanoparticles improves mechanical properties significantly. Similar improvements were noted in polypropylene/CNTs nanocomposites. High thermal conductivity of CNTs might increase heat input into polymer and enhance rate of burning. However, contradict this observation in CNTs. Examples of applications include reduction of fire risk in enclosed spaces in vehicles, submarines, aeroplanes, and ships [11]. The fire retardant behavior of polymers is a major challenge for extending their use to most applications. Nanocomposites are very attractive due to the fact that small amount of nanostructure can lead to great improvement in fire resistant property of nanocomposite [19].

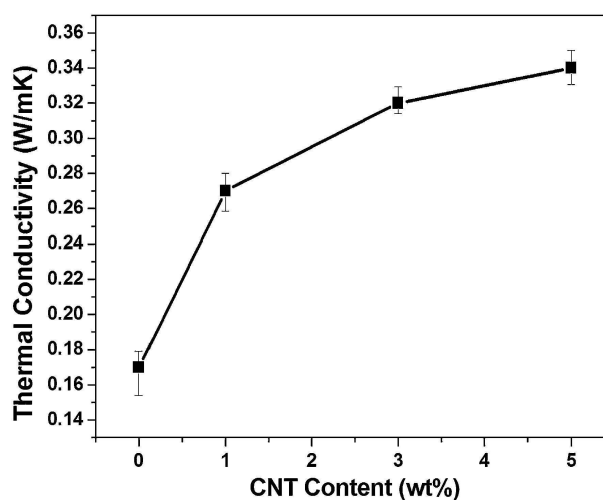


Figure 4.3: Variation of thermal conductivity with CNT content (wt per cent)

4.7 Sensors

Chemical sensors based on individual Single-wall nanotubes (SWNTs). They found that electrical resistance of a semiconducting single-wall nanotubes changed dramatically upon exposure to gas molecules such as NO_2 or NH_3 . The existing electrical sensor materials including carbon black polymer composites operate at high temperatures for substantial sensitivity whereas the sensors based on SWNT exhibited a fast response and higher sensitivity at room temperature.

A controlled method of producing free-standing nanotube-polymer composite films that can be used to form nanosensor [11].

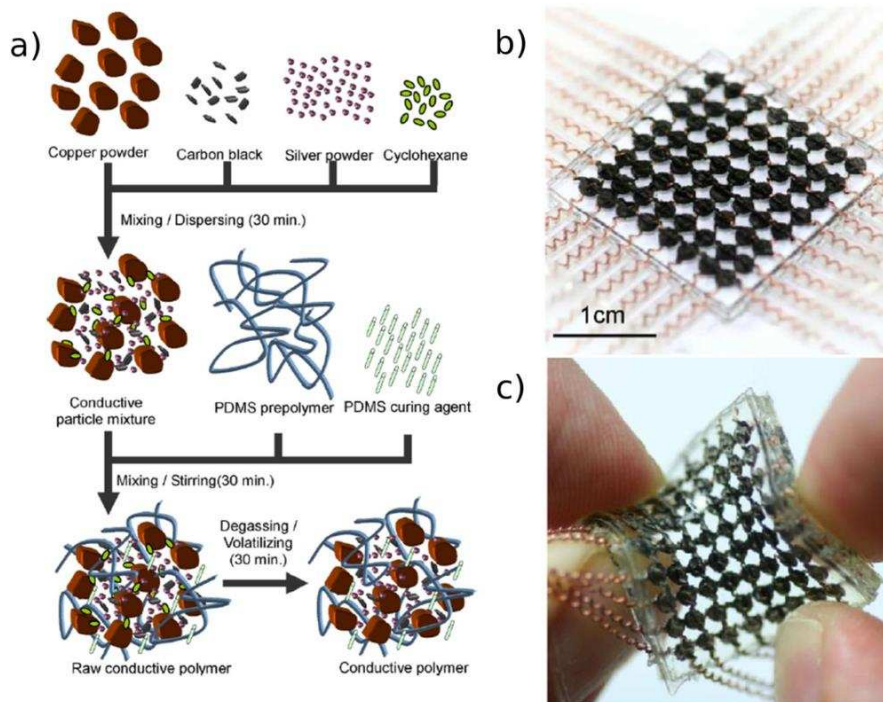


Figure 4.4: (a) Process flow of the preparation of the piezoresistive composite. (b) Image of the whole sensor showing each tactels composed by the composite disposed at the intersection between the spiral electrodes. (c) Example of the high stretchability and twistability of the sensor.

4.8 Actuators

Nanocomposite-based actuators have reduced power requirements and linear motion directly. A small amount (<5 vol per cent) CNTs in a polyurethane thermoplastic polymer, the resultant nanocomposite could store (and release when required) 50 per cent more strain energy than the unreinforced polymer. The addition of CNTs allowed indirect (infrared) or direct (Joule heating) activation. Compared to conventional additives (e.g. carbon black), considerable lower additions of CNTs was required. Existing shape memory polymers are insufficiently strong (low recovery stress) to find wider application. By adding a mechanical restraint in the form of inert silicon carbide nanoparticles to a commercial shape memory polymer, able to increase the recovery stress by 50 per cent, without degrading other properties. Can produce a composite material with embedded and aligned CNTs with an effective dielectric anisotropy, many orders of magnitude higher than in the usual liquid crystals. [11].

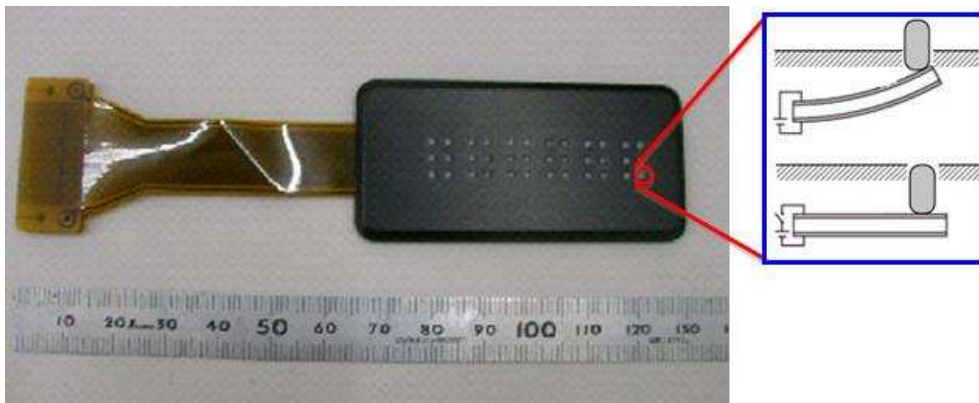


Figure 4.5: Braille System using carbon nanotube-polymer actuators

4.9 Automotive

Nanocomposites are an emerging class of polymeric materials exhibiting excellent mechanical properties, enhanced modulus and dimensional stability, flame retardancy, improved scratch and more resistance, superior thermal and processing properties, reduced war-page of components and enhanced impact resistance making them suitable to replace metals in automotive and other applications . The key drivers for the use of polymer nanocomposite-enabled parts in the automotive industry are reduction in vehicle's weight, improved engine efficiency (fuel saving), reduction in CO_2 emissions and superior performance (greater safety, increased comfort and better drive ability). The commercialization of polymer nanocomposites started in 1991 when Toyota Motor Co. first introduced nylon-6/clay nanocomposites in the market to produce timing belt covers as a part of the engine for their Toyota Camry cars. In 2002, General Motors launched a step-assist automotive component made of polyolefin reinforced with 3 *percent* nanoclays. The automotive industry can benefit from polymer nanocomposites in several applications such as engines and power train, suspension and breaking systems, exhaust systems and catalytic converters, frames and body parts, paints and coatings, lubrication, tires, and electric and electronic equipment. Since then, extensive research in nanocomposites field has been carried out worldwide [20].



Figure 4.6: parts of car(Automotive), that nanocomposites are used in it

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