CHAPTER 2

REVIEW OF LITERATURE

2.1 NANOTECHNLOGY

Nanotechnology which encompasses nanoscale science, engineering and technology is the understanding, control and manipulation of matter at the nanoscale. It covers the design, construction and utilization of functional structures with at least one characteristic dimension measured in nanometres (1 to 100 nanometres). Materials and systems designed using nanotechnology exhibits novel and significantly improved structural, mechanical, chemical and biological properties, phenomena and processes as a result of the limited size of their constituent particles or molecules [28-31]. The commonly used term “nanometre” is one billionth of a meter i.e. 1nm = 10^{-9} m. The basic visionary ideas for the evolution of nanotechnology were given by Richard Feynman in a lecture titled “There’s Plenty of Room at the Bottom,” at the annual meeting of the American Physical Society at the California Institute of Technology (Caltech) on December 29, 1959.

The term ‘‘nanotechnology’’ was coined and defined in the mid-1970^{s} in a paper presented by Norio Taniguchi [32]. He suggested that it is the processing of, separation, consolidation, and deformation of materials by one atom or one molecule. Subsequently, this basic definition was explored in greater depth by Eric Drexler [33]. He suggested an alternate way of producing things, by assembling things from the bottom, also known as molecular nanotechnology. He also vigorously promoted the technological significance of nanoscale phenomena and devices. As the possibilities of molecular nanotechnology grew and excitement built in the scientific community, many researchers began using the term for their own accomplishments at the nanoscale, distinct to molecular manufacturing.

Because of its small size of nano material the number of surface atoms become significant. The smaller the radius of the particle, the bigger is the fraction of surface atoms. For a spherical particle, the surface area $A_s = 4\pi r^2$, whereas the volume of the particle is $V = (4/3)\ \pi r^3$. Thus, the surface area-to-volume ratio is $A_s/V = 3/r$, and since the number of surface atoms is proportional to the area exposed, then this ratio is proportional to the fraction of surface atoms in the particle. The smallest closed packed cluster of spherical atoms is a 13-atom cluster wherein one atom is surrounded by 12 surface atoms (its coordination number). Here, the surface-to-volume ratio of atoms is very large at 92.3% (or 12/13). A 100-particle cluster will have a surface-to-volume ratio of 68.0%; a thousand, 38.4%; and a million, 4.4%. Indeed, the nanometer-sized cluster will have significant surface energy.

2.1.1 Developments in nanotechnology

Research and development areas of nanotechnology are, for example

- Analytics: Improving sensor properties and instruments for analysis, nano analysis using nano-chemical sensors
- Electronics: Chip production, manufacture of improved storage media
- Optoelectronics: New circuit design principles, making quantum effects usable for the production of new kinds of transistors, new kinds of semiconductor light sources.
- Optics: Ultra high precision processing of optical components, lithography for producing ever smaller electronic components, optical components with function surfaces (a spheres) for data projectors, cameras, spectacle lenses, scanners.
- Biotechnology and medicine: Use of nano-particles in the fight against tumours, nano-structured and functionalized surfaces and membranes, improved diagnosis and more targeted use of active agents; neuro-active implants
- Material science: Ultrafine nano-layers, nano-crystals, nano-structures for microelectronic components, fuel cells, scratch-proof surfaces, water and dirt repellent surfaces; antireflective properties, photoactive radiation.

The following overview shows some of the products already available:

1. Sun cremes with higher UV protection and for the more sensitive skin contain oxide particles
2. Cosmetics with nano-particles
3. Nano-scale ink particles for copiers and printers
4. Paints and coatings that absorb UV rays
5. Scratch-proof car paints

6. Textiles that are water and dirt repellent
7. Textiles that have improved sun protection owing to oxide particles
8. Safety clothing that prevents the build-up of static
9. Improved antireflection coating and greater scratch resistance in spectacle lenses
10. Optimized electronic chips, hard disks, RAM memory, diode lasers and displays.

2.1.2 Nanotechnology in textile

The textile industry has been already impacted by nanotechnology. Research involving nanotechnologies to improve performances or to create unprecedented functions of textile materials are flourishing. These research endeavours is mainly focused on using nano-size substances and generating nanostructures during manufacturing and finishing processes. Researchers all around the world looking at all sorts of metal additives and polymer additives, inorganic, organic materials to take them at nanoscale to impart lots of interesting properties to textiles. Nano-particles in functional textile finishing are thus widely reported [34-40].

In some typical textile finishing applications nano-particles can be substantially alter surface properties and also confer different functions to the textile materials as per Li, Lokyuen and Junyan [3]. As quoted by Wang, et.al [41] in their study in 2004 that nano particles have large surface area to volume ratio, which makes it easy for them to attach to fiber or fabrics, and increase the durability of the functions imparted by the particles. In addition, the coatings of nano particles do not affect the breathability, and hand feel of the textile. The commonest functions are wrinkle resistance, stain, soil and water repellency and anti static, anti bacterial and ultraviolet protection.

Over the past few years, a little word with big potential has been rapidly introducing itself into the world's consciousness. That word is "Nano" and mostly used in nanotechnology. Because of scientific convergence of physics, chemistry, biology, materials and engineering at nano scale, it is truly a portal opening on a new world. K Eric Drexler, mentioned word ‘Nanotechnology’ in 1986 in his famous book ‘Engines of Creation: The coming Era of Nanotechnology’ to describe what later became known as Molecular Nanotechnology (MNT), following up on visionary ideas presented 34 years earlier by famed physicist, Richard Feynman. As the possibilities of molecular nanotechnology grew and excitement built in the scientific community, many researchers began using the term for their own accomplishments at the nano-scale, distinct to molecular manufacturing.

The first work on nanotechnology in textiles was commercially undertaken by Nano-Tex, a subsidiary of the US-based Burlington Industries. Later, more and more textile companies began to invest in the development of nanotechnologies.

Nanotechnology is all about making products from very small constituents, components or subsystems to gain greatly enhanced material properties and functionality. One area where innovation is proceeding at a very fast pace is miniaturization. High levels of miniaturization is achieved by the emerging field of nanotechnology ability to work in the molecular level atom by atom, to create a large structures with fundamentally new properties and functionalities, with nano finishing. Nano finishing is concerned with positive control and processing technologies in the sub nanometer range [42]. Coating is a common technique used to apply nano-particles onto textiles. The coating compositions that can modify the surface of textiles are usually composed of nano-particles, a surfactant, ingredients and a carrier medium [43]. Several methods can apply coating onto fabrics, including spraying, transfer printing, washing, rinsing and padding [42]. Out of these methods, padding method is the most commonly used. The nano-particles are attached to the fabrics with the use of a padder adjusted to suitable pressure and speed, followed by drying and curing. The properties imparted to textiles using nanotechnology include high strength, toughness, water repellence, soil resistance, wrinkle resistance, anti-bacteria, anti-static, UV-protection, flame retardation, improvement of dyeability and so on [42].

Nanotechnology has real commercial potential for the textile industry due to the fact that conventional materials and methods used to impart different properties to fabrics often do not lead to permanent effects, and will lose their functions after laundering or wearing. Nano-structured composite fibers are the area where the early blooming of nanotechnology: Those composite fibers employ nano-size fillers as nanoparticles (such as clay, metal oxides, carbon black, etc.), graphite nanofibers (GNF) and carbon nanotubes (CNT). Besides, nano-structured composite fibers can be generated through foam-forming processes.

The main function of nano-size fillers is to increase the mechanical strength and improve the physical properties such as conductivity and antistatic behaviours. Due to their large surface area, these nanofillers have a better interaction with polymer matrices. Being in the nanometre range, the fillers might interfere with polymer chain movement and thus reduce the chain mobility. Being evenly distributed in polymer matrices, nanoparticles can carry load and increase the toughness and abrasion resistance; nanofibers transfers stress from polymer matrix and enhance tensile strength of composite fibers.

Additional physical and chemical performances imparted to composite fibers vary with specific properties of the nano fillers used. Distribution of nano fillers in polymer matrices through mechanical and chemical approaches is one of the important aspects leading to high quality of nanostructured composite fibers. Although some of the filler particles such as clay, metal oxides, and carbon black have previously been used as microfillers in composite materials for decades, reduction of their size into nanometre range have resulted in higher performances and generated new market interest.

The impact of nanotechnology in textile finishing area has brought up innovative finishes as well as new application technique. Particular attention has been paid in making chemical finishing more controllable. Ideally, discrete molecules or nanoparticles of finishes can be brought individually to designated sites on textile materials in a specific orientation and trajectory through thermodynamic, electrostatic or other technical approaches.

2.1.2.1 Significance of nanoparticles

The beauty of nano material lies in their size and shape. The change in properties of nano materials depend on two main factors. First, due to their dimensions, nanoparticles have large surface area when compared to the same mass of material produced in larger form. This can make the nano materials more chemical reactive and affect their strength or electric properties while second is the quantum effects that come into play at nano scale, can affect the structural, mechanical, optical, electric and magnetic properties of the material. The combinations of these two factors give to nanoparticles extraordinary unprecedented properties and behavior.

Nanotechnology can be used to change and improve the mechanical properties of textile fibers according to the corresponding application. Such properties include increased tensile strength, elasticity or fiber stiffness collectively stated by Hagenmueller, et al., 2003; Poncharal, et al., 1999; Stegmaier, 2006; Kalarikkal, Sankar, and Ifju, 2006 [12-15]. These properties can lead to the production of stronger or more elastic textiles or increase the tear and wear resistance of a fabric.

Nanoparticles presently of interest in the textile sector are metals, metal oxides, silicates, carbon products like graphite and carbon nano tubes (CNTs), but also organic materials are under investigation. They can be used either as filler to obtain nanocomposite fibers or deposited onto the textile surface. Adding nanoparticles to natural and man-made fibers to obtain nano composites give products with still higher performances like improved strength, chemical or abrasion resistance, water repellence, transpiration, fire resistance, antibacterial properties, UV protection, electrical conductivity.

Metals and metal oxides are important classes of nano-materials. Among the metals those attracting the highest interest are at the moment, copper [44] (Cu), silver [45] (Ag) and gold (Au) while among metal oxides can be cited silica (SiO_2), titania (TiO_2), alumina (Al_2O_3), iron oxide (Fe_3O_4, FeO) and zinc oxide (ZnO). ZnO nanoparticles that have been shown to provide UV shielding and reduced static electricity of nylon fiber [46]. TiO_2 /MgO nanoparticles that have shown to provide self sterilizing function. Nano size particles of Pd/Pt, Ag and Fe can be applied on textiles to impart antibacterial, conductive magnetic properties and remote heating properties. Nano size particles of TiO_2, ZnO, Al_2O_3, and MgO are a group of metal oxide that posses photo catalytic ability, electrical conductivity, UV absorption, and photo-oxidizing capacity against chemical and biological species. Clay nanoparticles possess electrical properties, fire, chemical and water resistance, ability of blocking UV light, giving to composite fibers reinforced with them specific properties such as flame retardant and anticorrosive behaviors. Another application of clay nanoparticles is to introduce dye attracting sites and creating dye holding space in polypropylene fibers, which are characterized by structural compactness and lack of dye attracting sites. As a result, the polypropylene can be coloured by acid dyes and disperse dyes.

The probably most investigated way of improving the mechanical properties of textiles trough nanoengineering is the integration of CNT which was found to increase tensile strength or elasticity significantly as observed by Chang, et al., 2005; Hagenmueller, et al.,2003; Dalton, et al.,2004; Poncharal, et al., 1999; Miaudet, et al.,2005 [12-18]. Hagenmueller, et al., 2003 [12] stated that CNT reinforced fibers were produced by melt compounding CNT with polystyrene (PS) and polypropylene (PP) or the production of a CNT-PP Masterbatch, Chang, et al., 2005 [16], both followed by melt spinning. Miaudet, et al., 2005 [18] uses the co-flowing of a CNT dispersion during solution spinning to produce reinforced polyvinyl-alcohol (PVA) fibers. Dalton, et al., 2004 [17] reports the production of PVA-CNT-composite fibers with increased strength by a modified solution spinning process. CNT can also be applied to the fabric by spray-coating or simply dipping the textile into a CNT solution Hecht, Hu, and Gruner, 2007 [19]. Mahltig, Haufe, and Bottcher, 2005 [22] furthermore reports the possibility to increase the abrasion stability of polyester by treating the finished fabric with a SiO_2 coating. The coating is produced trough a sol-gel process which involves the production of a nanoparticulate SiO_2 dispersion.

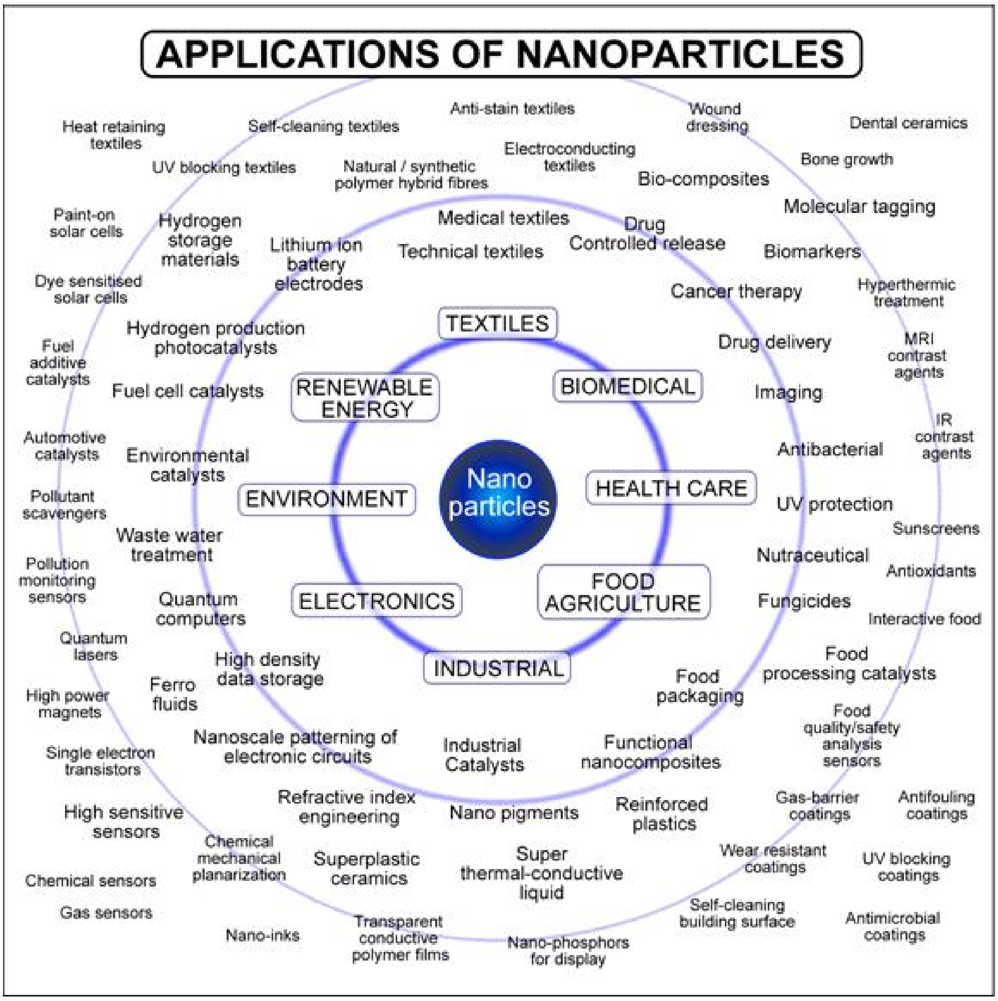

Figure 2.1 Applications of nanoparticles

Source: http://www.deakin.edu.au/research/ifm/research/nanoparticles.php [47]

2.1.2.2 Silica

The chemical compound silicon dioxide, also known as silica (from the Latin *silex*), is an oxide of silicon with the chemical formula SiO_2. It has been known for its hardness since antiquity. Silica is most commonly found in nature as sand or quartz, as well as in the cell walls of diatoms. Silica is manufactured in several forms including fused quartz, crystal, fumed silica, colloidal silica, silica gel, and aerogel [48].

Silica is the common name for materials composed of silicon dioxide (SiO_2) and occurs in crystalline and amorphous forms. Crystalline silica exists in multiple forms. Quartz and more specifically a-quartz is a widespread and well-known material. Upon heating, a-quartz is transformed into b-quartz, trydimite and cristobalite. Porosil is the family name for porous crystalline silica. Quartz exists in natural and synthetic forms, whereas all porosils are synthetic. Amorphous silica can be divided into natural specimens (e.g., diatomaceous earth, opal and silica glass) and human-made products [49].

Silicon dioxide is formed when silicon is exposed to oxygen (or air). A very shallow layer (approximately 1 nm or 10 Å) of so-called native oxide is formed on the surface when silicon is exposed to air under ambient conditions. Higher temperatures and alternative environments are used to grow well-controlled layers of silicon dioxide on silicon, for example at temperatures between 600 and 1200°C, using so-called dry or wet oxidation with O_2 or H_2O, respectively. The depth of the layer of silicon replaced by the dioxide is 44% of the depth of the silicon dioxide layer produced [50].

2.1.2.3 Application of nano-sized SiO_2

Silica is used primarily in the production of glass for windows, drinking glasses, beverage bottles, and many other uses. The majority of optical fibers for telecommunications are also made from silica. It is a primary raw material for many white ware ceramics such as earthenware, stoneware, porcelain, as well as industrial Portland cement. Silica is a common additive in the production of foods, where it is used primarily as a flow agent in powdered foods, or to absorb water in hygroscopic applications. It is the primary component of diatomaceous earth which has many uses ranging from filtration to insect control. It is also the primary component of rice husk ash which is used, for example, in filtration and cement manufacturing.

Thin films of silica grown on silicon wafers via thermal oxidation methods can be quite beneficial in microelectronics, where they act as electric with high chemical stability. In electrical applications, it can protect the silicon, store charge, block current, and even act as a controlled pathway to limit current flow. A silica-based aerogel was used in the Stardust spacecraft to collect extraterrestrial particles. Silica is also used in the extraction of DNA and RNA due to its ability to bind to the nucleic acids under the presence of chaotropes. As hydrophobic silica it is used as a defoamer component. In hydrated form, it is used in toothpaste as a hard abrasive to remove tooth plaque. In its capacity as a refractory, it is useful in fiber form as a high-temperature thermal protection fabric. In cosmetics, it is useful for its light-diffusing properties and natural absorbency. Colloidal silica is used as a wine and juice fining agent. In pharmaceutical products, silica aids powder flow when tablets are formed. Finally, it is used as a thermal enhancement compound in ground source heat pump industry. Also they use in textile for achieving the multi functional properties of the fabric [51, 52].

Since one of the primary reasons for adding inorganic fillers to polymers is to improve their mechanical performance [53], the mechanical properties of polymer nanocomposites are most concerned [54, 55]. It is well-known that one of the major requirements of polymer nanocomposites is to optimize the balance between the strength/stiffness and the toughness as much as possible [67]. Therefore, it is usually necessary to characterize the mechanical properties of nanocomposites from different viewpoints. Several criteria, including tensile strength, impact strength, flexural strength, hardness, fracture toughness, and so forth, have been used to evaluate the nanocomposites. Tensile test is the most widely used method to evaluate the mechanical properties of the resultant nanocomposites, and accordingly Young’s modulus, tensile strength, and the elongation at break are three main parameters obtained. These vary with the silica content, but the variation trends are different. Furthermore, impact test is also widely used for the mechanical properties characterization.

2.2 COMPOSITE MATERIALS

Composite materials are engineered materials made from two or more constituent material that remains separate and distinct on a macroscopic level while forming a single component. Composite materials are formed by combining two or more material that has quite different properties. The different materials work together to give the composite unique properties, but within the composite you can easily apart the materials. They do not dissolve or blend into each other.

Textile materials play critical role in the manufacture of advanced composite materials in the form of high performance fibres, hybrid yarns and pre-forms. The high performance fibres provide the basic reinforcement in the form of high strength and modulus to the materials. The biggest advantage of modern composite materials is that they are light as well as strong. By choosing an appropriate combination of matrix and reinforcement material, a new material can be made that exactly meets the requirements of a particular application. Composites also provide design flexibility because many of them can be molded into complex shapes. The downside is often the cost. Although the resulting product is more efficient, the raw materials are often expensive [1].

2.2.1 Nanocomposite materials

When inorganic phases in organic/inorganic composites used in nanosize, they are called as nanocomposites. Organic/inorganic nanocomposites are generally organic polymer composites with inorganic nanoscale building blocks. They combine the advantages of the inorganic material (e.g., rigidity, thermal stability) and the organic polymer (e.g., flexibility, dielectric, ductility, and processability). Moreover, they usually also contain special properties of nanofillers leading to materials with improved properties. A defining feature of polymer nanocomposites is that the small size of the fillers leads to a dramatic increase in interfacial area as compared with traditional composites. This interfacial area creates a significant volume fraction of interfacial polymer with properties different from the bulk polymer even at low loadings [53, 57-65].

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2.2.2 Polymer nanocomposite

Conventional polymer composites, usually reinforced by micrometer-scale fillers into polymer matrices, have found large-scale applications for decades in automobile, construction, electronics, and consumer products. Composites gain enhanced properties such as higher strength and stiffness compared with neat polymer [66, 67]. However, properties achieved by these traditional composites involve compromises. For example, stiffness is obtained at cost of toughness. Recently, nanoscale filled polymer composites or polymer nanocomposites gave a new way to overcome the limitations of traditional counterparts.

A nanocomposite is defined as a composite material where at least one of the dimensions of one of its constituents remains on the nanometre size scale. The term usually also implies the combination of two (or more) distinct materials, such as a ceramic and a polymer, rather than spontaneously phase-segregated structures [68]. Polymer nanocomposite is an emerging class of mineral-filled polymer that contain relatively small amount (usually <10%) of nanometre-sized inorganic particles. The introduction of inorganic nanoparticles as additives into polymer systems has resulted in polymer nanocomposites (PNs). They exhibit multifunctional, high-performance polymer characteristics beyond what traditional filled polymeric materials possess. The three major characteristics that define and form the basis of polymer nanocomposite performance are: nanoscopically-confined matrix of polymer; nanoscale inorganic constituents; and nanoscale arrangement of the nanoscale constituents [69].

2.2.3 Types of polymer nanocomposites

Methods of synthesis which have effect on controlling particle size distribution, dispersion, and interfacial interactions are critical for realizing the novel properties of polymer nanocomposites. Synthesis techniques for nanocomposites are quite different from those for conventional microscale-filled composites. One universal technique for preparing polymer nanocomposites can be developed. But it becomes impossible due to the physiochemical differences between each system. Each polymer system may require a special set of processing conditions to be formed and different synthetic techniques in general could yield non-equivalent results [70].

Polymer nanocomposites are prepared by mixing a polymer (or monomer) with dissimilar material or additives that have one or more dimensions on the nanometre scale. Among several factors in selecting a method of synthesis, the most prominent to be considered is geometry of the nanofillers. They are generally classified into three categories, viz. 1) One dimensional (1D) nanotube fillers, which have one diameter less than 100 nm and an aspect ratio of more than 100, such as carbon nanotubes (CNTs) first noticed in 1991 by Sumio Iijima [71]; 2) 2D plate-like nanofillers, typically defined as layered materials with a thickness on the order of 1nm and an aspect ratio in the other two dimensions of at least 25 such as layered silicate; 3) Nanopowders (3D), which are equi-axed particles with less than 100 nm in their largest dimension such as nanosilica. The following subsections present a variety of synthesis methods.

2.2.3.1 Polymer / Nanotube Composites

The synthesis of polymer nanotube composites is still in its infancy and the most common nanotubes used are carbon nanotubes which include multi-walled nanotube (MWNT) and single-walled nanotube (SWNT). CNTs are exceptionally stiff and strong materials which are able to be tailored into polymers to make composites with improved mechanical and electrical properties. However, strong van der Waals forces which lead to agglomerate and poor solubility in most solvents hinder their potential applications.

To tackle this obstacle, the physical and/or chemical modification of the surface of CNTs with or without the aid of surfactants is one effective approach in achieving good dispersion of CNTs into a polymer. Physical modification has poor miscibility and the resulted dispersions often re-agglomerate in time. Chemical modification becomes an increasing way to functionalize CNTs.

In-situ polymerization of a monomer in pre-modified CNTs is the most common synthetic strategy studied by many researchers to develop good polymer nanocomposites [71-75]. Direct mixing is another technique that has been used to make polymer nanotube composites [76-80].

2.2.3.2 Polymer / Layered Nanofiller Composites

The most common 2D fillers are layered silicates (LS), well known as clay including mica and talc. Two challenges are being faced in developing this type of nanocomposites: i) Dispersion of the LS in polymers is hindered by the inherent tendency to form face-to-face agglomerates due to high interlayer energy; and ii) Hydrophilic LS are incompatible with hydrophobic polymers. To solve these problems, treatment or functionalization of LS is usual routine to weaken interlayer cohesive energy. Thereby, it can expand the LS galleries, and to match the polarity of the LS surface to the polymer, thus improving compatibility between them. Depending on different extents of dispersion of the LS in a monomer or polymer, three types of composites can be formed as illustrated in figure 2.3 [81]. The first type is an immiscible conventional composite in which the polymer is unable to intercalate between the LS forming a poorly dispersed phase separated composite. The second type is intercalated polymer layered silicates (PLS) nanocomposite in which a single, extended polymer chain is intercalated between the silicate layers resulting in a well ordered multilayer with a distance of a few nanometres. The third type is exfoliated PLS nanocomposites in which the silicate layers are ultrafinely dispersed in a continuous polymer matrix. Exfoliated is the most desirable system which shows unlimited solvability [81].

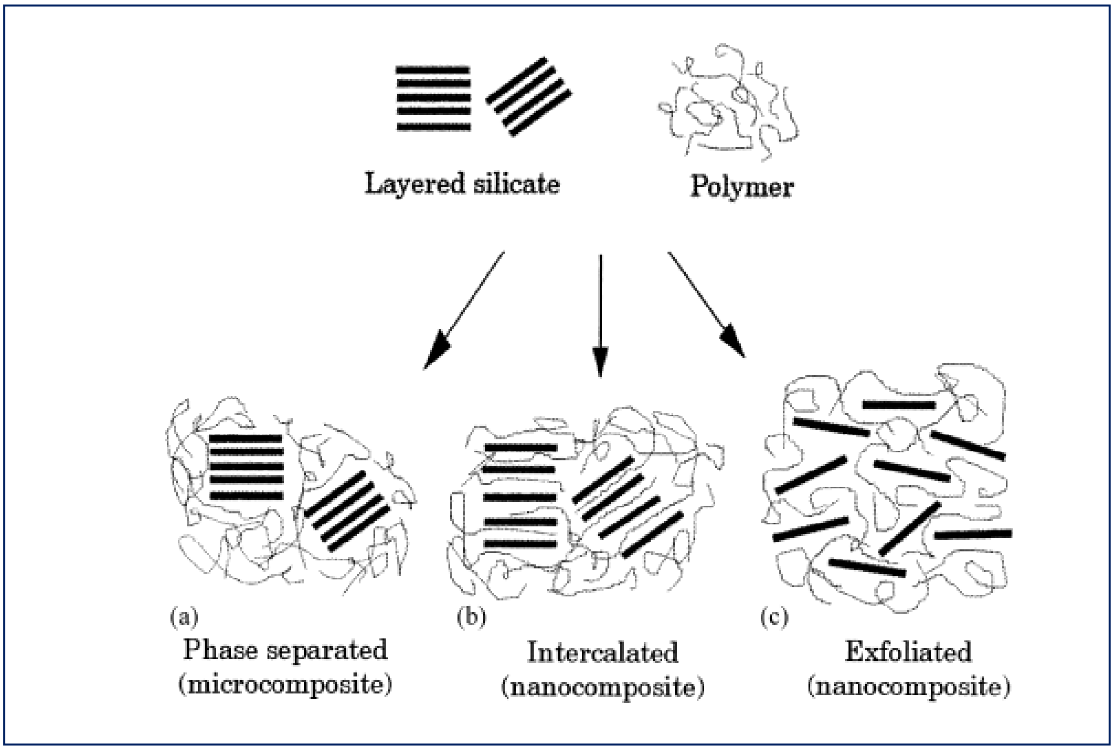


Figure 2.2 Illustration of different types of polymer layered silicates (PLS) composites.

Source: Alexandre et al. [81], 2000.

The synthesis of PLS nanocomposites involve the following approaches; the first approach is to intercalate the pre-treated LS with a suitable monomer or precursor followed by *in-situ* polymerization, which is called *in-situ* polymerization route. The second approach is called as solution intercalation route and involves dissolving a polymer and the LS in a compatible polymer-silicate solvent. The third method is melt intercalation route, which involves mixing the LS with the polymer matrix in the molten state. If the layer surfaces are sufficiently compatible with the chosen polymer, the polymer can crawl into the interlayer space and form either an intercalated or an exfoliated nanocomposite. As no solvent is required, this route is the preferred process with respect to environmental and economical issues. Fourth approach is template synthesis method; in this silicates are formed *in situ* in aqueous solution containing the polymer and the silicates building blocks. This approach is mostly used for double layered hydroxide based silicates but is less developed for LS.

2.2.3.3 Polymer / Nanopowder Composites

Nanopowders primarily involve metals, semiconductors, metal oxides. Generally, the dispersion of nanopowders in polymers is carried out by three methods. The first is direct mixing or blending of the polymer and the nanopowder either as discrete phases (known as melt mixing) or in solution (solution mixing) [82]. The second is sol-gel process which starts with molecular precursor at ambient temperature and then forms metal or metal oxide framework by hydrolysis and condensation. The third is *in-situ* grafting polymerization of macromolecular chains on the surface of nanopowder. All of these approaches share a common theme, the intermingling on the nanometre scale of dissimilar materials with properties not available from either of the component pure materials [83].

2.2.3.3.1 Direct Mixing

Melt mixing is the fastest method for introducing new nanocomposites to market since it can take full advantage of well-built polymer processing equipments including extruders or injectors. Although being successful in many cases, melt mixing method has several drawbacks. First, this process only builds up relatively weak interaction force between the polymer and the nanopowder. Nanopowders have a very strong tendency to aggregate and the dispersion was successfully achieved only after modification of the surface of inorganic nanopowders. Second, for some polymers, this processing method may be limited due to rapid increase of the viscosity with the addition of a few volume fractions of nanopowders [83].

2.2.3.3.2 Sol-Gel Processing

The sol-gel processing of the nanopowders inside the polymer dissolved in non-aqueous or aqueous solution is the ideal procedure for the formation of interpenetrating networks between inorganic and organic moieties at the milder temperature in improving good compatibility and building strong interfacial interaction between two phases. This process has been used successfully to prepare nanocomposites with silica, alumina, calcium oxide, titania in a range of polymer matrices [83].

2.2.3.3.3 Graft Polymerization

Another method for avoiding phase-separation is graft polymerization, where nanopowders are dispersed in the monomer or monomer solution. The resulting mixture is polymerized by standard polymerization methods. This process provides flexibility in our ability to engineer the powder surface being placed in composites. Besides tailoring specific properties in composites via relatively strong interaction, the layer of polymer bonded to the nanopowders can control aggregation of the nanopowders. There are two approaches for graft polymerization as shown in figure 2.4 [84]. One approach is “grafting to”, also termed "tethering", which consists of immobilization of polymerizable groups on the nanopowder surface for copolymerization. The other is “grafting from” approach, also known as surface-initiated polymerization, which involves grafting an initiator onto the nanopowder surface to form polymer chains from the surface.

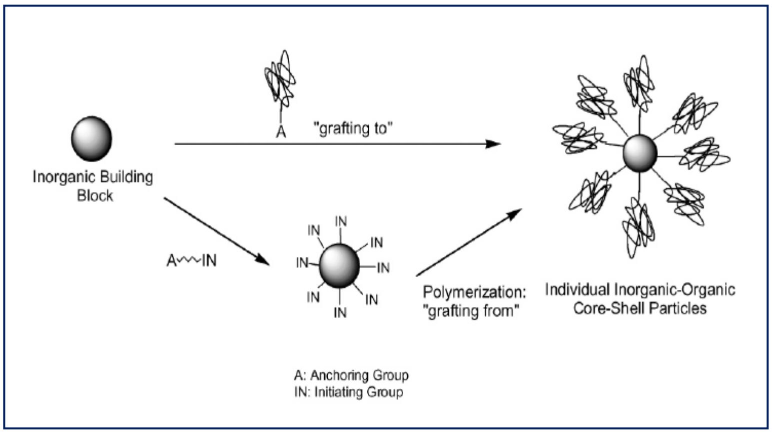


Figure 2.3 Two approaches of graft polymerization.

Source: Kichelbick [84], 2003.

2.3 PREPARATION OF NANOCOMPOSITE

Nanocomposite [85] can be prepared by following three synthesis routes. The organic component can be introduced as matrix:

- (i) A precursor, which can be a monomer or an oligomer,
- (ii) A preformed linear polymer (in molten, solution, or emulsion states), or
- (iii) A polymer network, physically (e.g., semicrystalline linear polymer) or chemically (e.g., thermosets, elastomers) cross-linked.

The mineral part can be reinforced as:

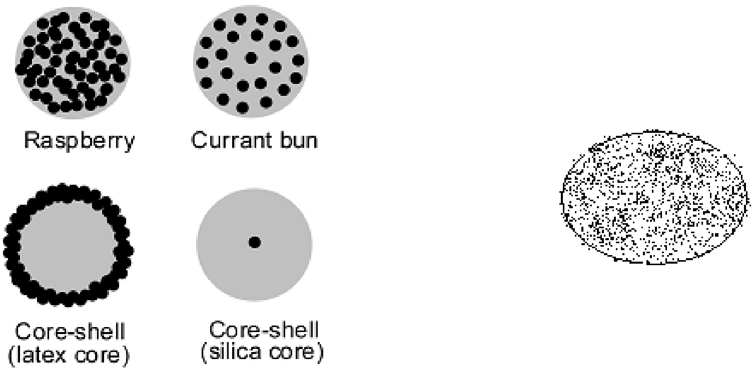
- (i) A precursor (e.g., silica, silver, etc.) or
- (ii) Preformed nanoparticles.

However, there are number of methods used to prepare polymer nanocomposite materials. The nanoparticles can be introduced to textiles at different stages such as:

1) Filament / film preparation stage
2) During finishing stage
3) During Garment processing

2.3.1 Filament / Film preparation stage

Sols can be used as basic solution for the spinning of fibres or during preparation of film. By this method, simple glass fibres are prepared by dry spinning of silica sols, quoted by Peltola et al.,2001; Celzard et al., 2002 [86, 87]. By spinning directly from appropriate sols, inorganic composite filaments or composite film can be prepared, not only based on pure SiO_2 but also on other metal oxides or mixtures of both. Amalvy, et. al [88] has basically described two different kinds of sol-gel based filaments: inorganic/organic or pure inorganic composite filaments, the schematic representation of the possible Nanocomposite particle morphologies as see below in figure.



Polymer/ silica composite silica composite

Figure 2.4 Schematic Representations of the Possible Nanocomposite Particle Morphologies

Polymer-based organic/inorganic nanocomposites have gained increasing attention in the field of materials science. Inorganic/organic nanocomposite materials combine the advantages of the inorganic material and the organic polymer. Various inorganic nanoscale materials including silicate, metal nano-particles, metal oxides, and semiconductors have been used to prepare polymer/inorganic nanocomposite materials.

In recent years, polymer/SiO_2 nanocomposites have attracted substantial academic and industrial interest. Many potential and practical applications of this type of nanocomposites in the fields of coatings, flame-retardant materials, and photo resist materials, and optical devices have been reported. There are essentially four different approaches to use for synthesize polymer-silica nanocomposites as stated by Jianan Zhang, et.al., in 2008 [89].

1) Melt intercalation
2) Solution method
3) In situ polymerization. From Ahmadi et al., 2004 [90]
4) Electro spinning. From http://www.worldscibooks.com/materialsci/6961.html [91].

2.3.2 Finishing stage

i) Pad-dry-cure and Spray finishing method:

The application of nanosols to the textile materials can be carried out by conventional procedures used for textile finishing. Such procedures are mainly simple dipping, padding or spraying processes, foam finishing. Even printing processes using nanosols can be realized on textiles. Probably the simplest method is dipping of a textile sample into the nanosol.

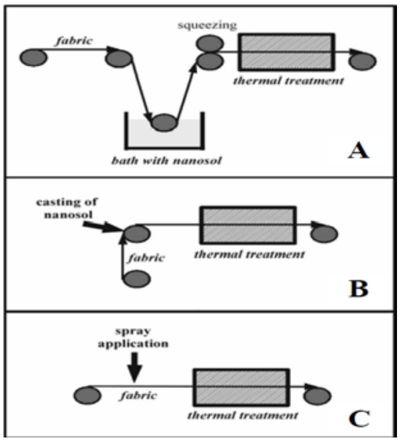


Figure 2.5 Schematic drawing of nanosol finishing of textiles by conventional application techniques, A: padding, B: casting, C: spraying.

Source: http: //217.218.200.220 /c/ document_library/ LFE-12410.pdf [92]

The fabric is immersed in the sol, remains there for a certain time, it is taken out and it either dries under the ambient conditions or it is thermally cured in an oven or a stenter frame. For certain applications or finishing full penetration of the textile by the sol is not necessary. As an example, repellence might only be needed on one side of the product. In these cases the sol application cannot be carried out by dipping or padding. For this the casting of the nanosol or a spray application treating only one side of the textile fabric is useful methods. The above mentioned application techniques are depicted schematically in Figure 2.5.

ii) Foam Finishing Method:

One important application method for chemical finishes is the use of foam to apply the finish to the fabric. By replacing part of the water in the chemical formulation with air, the amount of water added to the fabric can be significantly reduced. In addition, surfactants are included in the formulation to be foamed. Even if they are carefully selected, they may cause effect reduction of repellent finishes. The chemical formulation is mixed with air in a foam generator producing high volumes of foam that can be applied to fabrics in a number of ways. The ratio of liquid to air in foam is referred to as the ‘blow ratio’, Terlingen in 1993 [93] has conveniently determined by equation:

$$\text{blow ratio} = \frac{1}{\text{foam density}}$$

……………Equation 2.1

iii) Plasma Technology:

Before going on into the uses of plasma, it’s important to understand what it is. Simply put, plasma is nothing more than ionized gas. When a surface is exposed to plasma a mutual interaction between the gas and the substrate takes place. The surface of the substrate is bombarded with ions, electrons, radicals, neutrals and UV radiation from the plasma while volatile components from the surface contaminate the plasma and become a part of it, as per website “aasimahmed.files.wordpress.com/.../a-review-of-plasma-treatment-for-application-on-textile-substrate-aasim-ahmed.pdf” [94].

The electrons in the plasma are able to cleave covalent chemical bonding. Therefore, physical and chemical modification of surfaces of various substrates is possible. It is through the use of these in different combinations and on different substrate that the vast variety of outcomes which are possible through plasma treatment can be achieved. The mechanism of plasma modification is shown in figure 2.6.

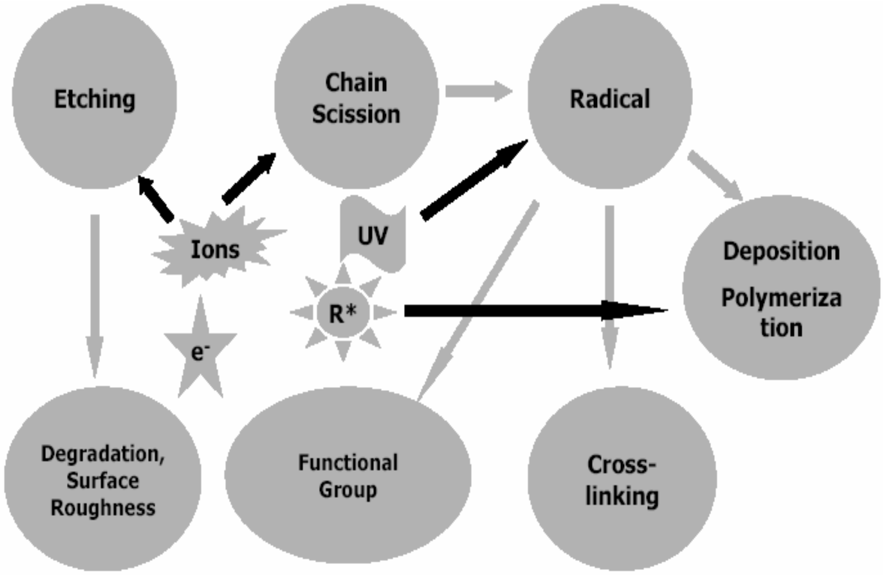


Figure 2.6 Mechanism of plasma-substrate interaction

Coating, deposition or polymerization Coating and layering are synonymous terms for applying films on textiles substrate by using plasma activated gasses. The main advantages of plasma treatment are the extremely short treatment time and low application temperatures; water or solvents respect to drying steps after plasma finishing can be avoided as per Hua Zou, et al., in 2008 [95].

2.3.3 Garment processing stage

Applying chemical finishes to garments is usually accomplished using exhaustible finishes (softeners, antimicrobials, ultra violet (UV) absorbers, and so on), which are added to the bath of the garment processing machine after all other garment wet processing steps have been completed. However, occasionally, a non-exhaustible finish such as an easy care finish is desired. Special procedures have been developed for this situation. One approach is to extract as much water as possible from the garments and then immerse them into the finish solution, either in a separate trough or in the garment machine itself, followed by further extraction, drying and curing. A second approach is to spray a precise amount of finish solution into the garment processing machine after water extraction. Even distribution of finish is accomplished by rotating the garments long enough to allow the finish to migrate throughout the garment. Drying and curing complete the process. Both methods have been demonstrated commercially, but the spray procedure requires fitting existing garment machines with the precision spraying attachment, while the immersion procedure involves less capital investment, but consumes more chemical finish [92].

2.4 TESTING AND ANALYSIS OF POLYMER NANOCOMPOSITE MATERIALS

The characterization methods used in the analysis of the chemical structure, microstructure and morphology, as well as the physical properties, of the nanocomposites are varied. To fully understand structure-property relationships, several characterization techniques are often employed. The properties of the nanocomposites strongly depend on their composition, the size of the particles, interfacial interaction, etc. The interfacial interaction between polymer and silica (which depends on the preparative procedure) strongly affects the mechanical, thermal, and other properties of the nanocomposites.

TEM, SEM, and AFM are three powerful microscopy techniques to observe the morphology of nanocomposites. Crystallization behaviors of the silica nanoparticle-filled composites are usually studied by DSC and XRD. The chemical structure of polymer/silica nanocomposites is generally identified by FTIR and solid-state NMR spectra. Thermal properties of materials are change with temperature. They are studied by thermal analysis techniques, which include DSC, TGA, DTA, dielectric thermal analysis, since one of the primary reasons for adding inorganic fillers to polymers is to improve their mechanical performance, and the mechanical properties of polymer nanocomposites are most concerned. Therefore, it is usually necessary to characterize the mechanical properties of nanocomposites from different viewpoints. Several criteria, including tensile strength, impact strength, flexural strength, hardness, fracture toughness, and so forth, have been used to evaluate the nanocomposites as per Russell, et al., in 2002 [96].

2.4.1 Structural analysis of nanocomposite materials

The structural features of nano material need to be determined in various stages of production such as distribution, surface structure and composition, which are critical to ensure the materials and structures are in nano scale to archive special properties as reported by Li, Lokyuen and Junyan in 2003 and also from website- *http://www.egr.msu.edu/cmsc/esem/index.html.;http://www.egr.msu.edu/cmsc/nano/index.html* [3, 84, 85]. Such structural feature can be characterized by a range of techniques and instruments such as Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), Scanning Tunneling Microscopy (STM), High Resolution Transmission Electron Microscopy (TEM), X-ray Photoelectron Spectroscopy (XPS), Auger Electron Spectroscopy (AES), Near Field Scanning Optical Microscopy (NSOM or SNOM), X-ray and Neutron Diffraction, Fourier transform infrared spectroscopy (FTIR) and other spectroscopic techniques.

The properties of nano materials and structures/composites also need to be measured to test whether specific and unique properties can be derived due to the nano scale structures. Properties characterization should be carried out in various aspects in relation to specific functions to be achieved such as in mechanical, thermal, electrochemical, optical properties.

Testing and analysis of nanocomposite materials is an emerging field posing lot of challenges to scientists and technologists. Thus, nanotechnology has motivated the upsurge in research activities on the discovery and invention of sophisticated characterization techniques to allow a better control on structures of composite materials in nano range. This section discusses the basic principle and applications of these instrumental techniques in the field of nanotechnology research in textiles.

2.4.1.1 Analysis by microscopy

Optical microscopes are generally used for observing micron level materials with reasonable resolution. Further magnification cannot be achieved through optical microscopes due to aberrations and limit in wavelength of light. Hence, the imaging techniques such as scanning electron microscopy (SEM), transmission electron microscopy (TEM/HRTEM), scanning tunneling microscopy (STM), atomic force microscopy (AFM), etc. have been developed to observe the sub micron size materials. Though the principles of all the techniques are different but one common thing is that they produce a highly magnified image of the surface or the bulk of the sample. Nanomaterials can only be observed through these imaging techniques as human eye as well as optical microscope cannot be used to see dimensions at nano level. Basic principles and applications of all these imaging techniques used in nanotechnology research are described below.

2.4.1.1.1 Scanning Electron Microscopy (SEM)

Structural phenomena play an important role in determining the properties of a polymer. Mechanical properties are determined not only by the changes in shape confirmation and by motion of individual molecules of the polymers, but also by the behaviour of larger and more complex structural formations.

The scanning electron microscope is an electron microscope that images the sample surface by scanning it with a high energy beam of electrons. Conventional light microscopes use a series of glass lenses to bend light waves and create a magnified image while the scanning electron microscope creates the magnified images by using electrons instead of light waves, as found on website http:// www.purdue.edu/ REM/rs/sem.htm [99].

Basic Principle:

When the beam of electrons strikes the surface of the When the beam of electrons strikes the surface of the specimen and interacts with the atoms of the sample, signals in the form of secondary electrons, back scattered electrons and characteristic X-rays are generated that contain information about the sample's surface topography, composition, etc. The SEM can produce very high-resolution images of a sample surface, revealing details about 1-5 nm in size in its primary detection mode i.e. secondary electron imaging. Characteristic X-rays are the second most common imaging mode for an SEM. These characteristic X-rays are used to identify the elemental composition of the sample by a technique known as energy dispersive X-ray (EDX). Back-scattered electrons (BSE) that come from the sample may also be used to form an image. BSE images are often used in analytical SEM along with the spectra made from the characteristic X-rays as clues to the elemental composition of the sample.

In a typical SEM, the beam passes through pairs of scanning coils or pairs of deflector plates in the electron column to the final lens, which deflect the beam horizontally and vertically so that it scans in a raster fashion over a rectangular area of the sample surface. Electronic devices are used to detect and amplify the signals and display them as an image on a cathode ray tube in which the raster scanning is synchronized with that of the microscope. The image displayed is therefore a distribution map of the intensity of the signal being emitted from the scanned area of the specimen.

Working:

SEM requires that the specimens should be conductive for the electron beam to scan the surface and that the electrons have a path to ground for conventional imaging. Non-conductive solid specimens are generally coated with a layer of conductive material by low vacuum sputter coating or high vacuum evaporation. This is done to prevent the accumulation of static electric charge on the specimen during electron irradiation. Non-conducting specimens may also be imaged uncoated using specialized SEM instrumentation such as the "Environmental SEM" (ESEM) or in field emission gun (FEG) SEM operated at low voltage, high vacuum or at low vacuum, high voltage.

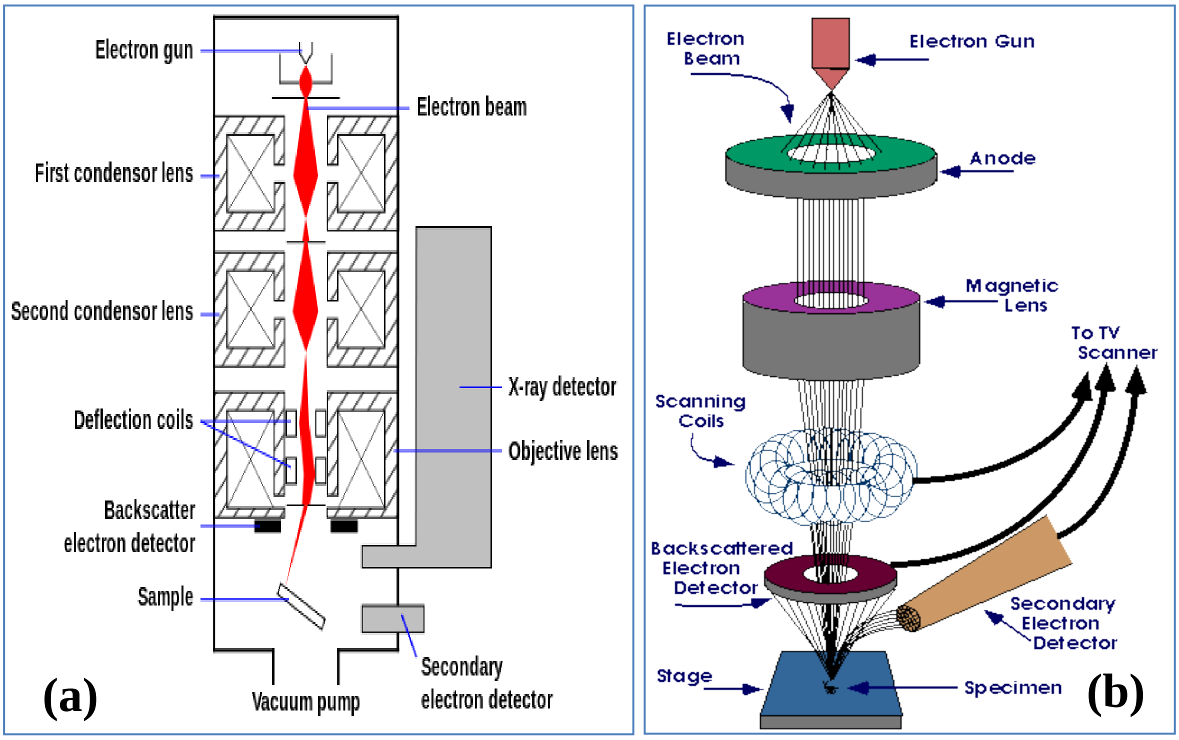


Figure 2.7 Schematic Diagram of Scanning Electron Microscope (a), (b) [100,101].

Applications:

The SEM shows very detailed three dimensional images at much high magnifications (up to x300000) as compared to light microscope (up to x 10000). But as the images are created without light waves, they are black and white. The surface structure of polymer nanocomposites, fracture surfaces, nanofibres, nano-particles and nanocoating can be imaged through SEM with great clarity. As very high resolution images of the dimension 1 - 5 nm can be obtained, SEM is the most suitable process to study the nanofibres and nanocoatings on polymeric/textile substrate as advocated by Joshi & Viswanathan in 2006; Joshi et al., 2006; Klajn et al.,2007 [102-104]. Marcato et al. in 2005 and Ma et al. in 2001 [105, 106] also, recommandes the SEM technique to view dispersion of nanoparticles in the bulk and on the surface of nanocomposite fibers and coatings on yarns and fabric samples.

2.4.1.1.2 Energy Dispersive X-ray Analysis (EDX)

Energy dispersive X-ray analysis is a technique to analyze near surface elements and estimate their proportion at different position, thus giving an overall mapping of the sample.

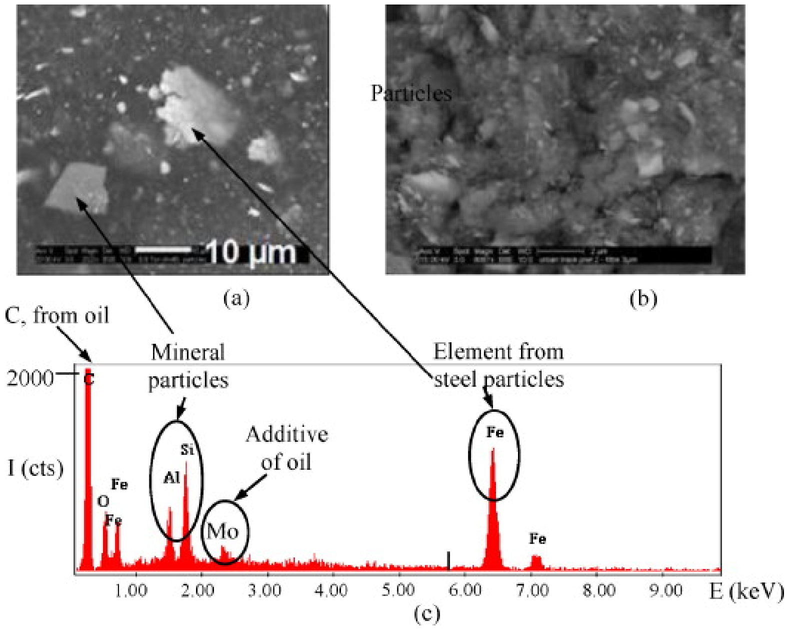


Figure 2.8 Elemental analysis of nanoparticles by EDX.

Basic Principle:

This technique is used in conjunction with SEM. An electron beam strikes the surface of a conducting sample. The energy of the beam is typically in the range 10-20keV. This causes X-rays to be emitted from the material. The energy of the X-rays emitted depends on the material under examination. The X-rays are generated in a region about 2 microns in depth, and thus EDX is not truly a surface science technique. By moving the electron beam across the material an image of each element in the sample can be obtained. Due to the low X-ray intensity, images usually take a number of hours to acquire.

Applications:

The composition or the amount of nano-particles near and at the surface can be estimated using the EDX, provided they contain some heavy metal ions. For example, the presence of Au, Pd and Ag nano-particles on surface can easily be identified using EDX technique. Elements of low atomic number are difficult to detect by EDX, The Si-Li detector protected by a beryllium window cannot detect elements below an atomic number of 11 (Na). In windowless systems, elements with as low atomic number as 4 (Be) can be detected. EDX spectra have to be taken by focusing the beam at different regions of the same sample to verify spatially uniform composition of the bimetallic materials. Figure shows the elemental analysis of nano-particles can be verified by EDX as reported by Sano et al. in 2002 [107].

2.4.1.1.3 Transmission Electron Microscopy (TEM)

Transmission electron microscopy is a microscopy technique whereby a beam of electrons is transmitted through an ultra thin specimen and interacts as passes through the sample. An image is formed from the electrons transmitted through the specimen, magnified and focused by an objective lens and appears on an imaging screen.

Basic Principle:

The contrast in a TEM image is not like the contrast in a light microscope image. In TEM, the crystalline sample interacts with the electron beam mostly by diffraction rather than by absorption. The intensity of the diffraction depends on the orientation of the planes of atoms in a crystal relative to the electron beam; at certain angles the electron beam is diffracted strongly from the axis of the incoming beam, while at other angles the beam is largely transmitted.

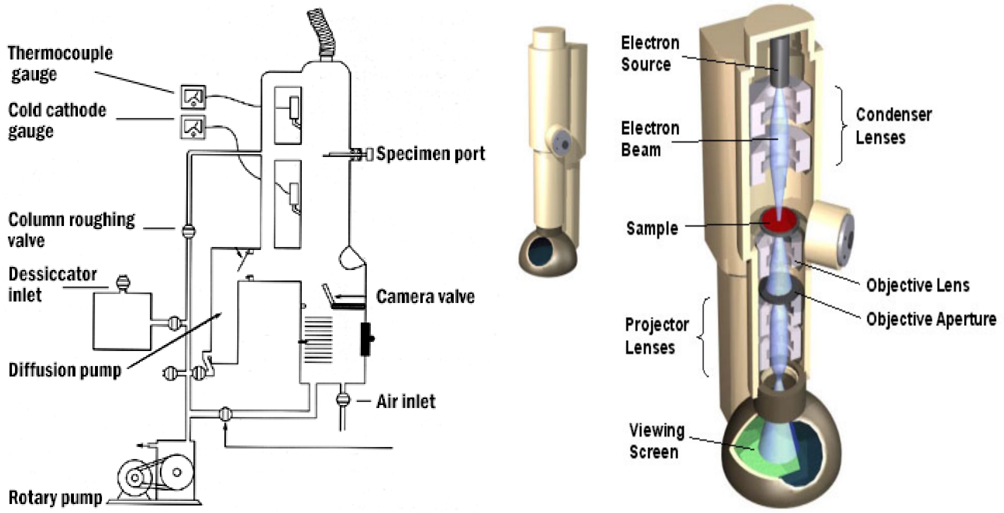


Figure 2.9 Schematic of a transmission electron microscope

Modern TEMs are equipped with specimen holders that allow to tilt the specimen to a range of angles in order to obtain specific diffraction conditions. Therefore, a high contrast image can be formed by blocking electrons deflected away from the optical axis of the microscope by placing the aperture to allow only unscattered electrons through this produces a variation in the electron intensity that reveals information on the crystal structure. This technique, particularly sensitive to extended crystal lattice defects, is known as 'bright field' or 'light field'. It is also possible to produce an image from electrons deflected by a particular crystal plane which is known as a dark field image.

The specimens must be prepared as a thin foil so that the electron beam can penetrate. Materials that have dimensions small enough to be electron transparent, such as powders or nanotubes, can be quickly produced by the deposition of a dilute sample containing the specimen onto support grids. As polymeric nanocomposites or the textile samples are not as hard as metals, they are cut into thin films (< 100 nm) using ultra-microtome with diamond knife at cryogenic condition (in liquid nitrogen).

Applications:

The TEM is used widely both in material science/metallurgy and biological sciences. In both cases the specimens must be very thin and able to withstand the high vacuum present inside the instrument. For biological specimens, the maximum specimen thickness is roughly 1 micrometer. To withstand the instrument vacuum, biological specimens are typically held at liquid nitrogen temperatures after embedding in vitreous ice, or fixated using a negative staining material such as uranyl acetate or by plastic embedding.

The properties of nanocomposites depend to a large extent on successful nano level dispersion or intercalation/exfoliation of nano particles, therefore monitoring their morphology and dispersion is very crucial. TEM images reveal the distribution and dispersion of nano-particles in polymer matrices of nanocomposite fibres, nano coatings, etc. The extent of exfoliation, intercalation and orientation of nano-particles can also be visualized using the TEM micrograph

2.4.1.1.4 High Resolution Transmission Electron Microscopy (HRTEM)

High resolution transmission electron microscopy is an imaging mode of the transmission electron microscope that allows the imaging of the crystallographic structure of a sample at an atomic scale.

Basic Principle:

As opposed to conventional microscopy, HRTEM does not use absorption by the sample for image formation, but the contrast arises from the interference in the image plane of the electron wave with itself. Each imaging electron interacts independently with the sample. As a result of the interaction with the sample, the electron wave passes through the imaging system of the microscope where it undergoes further phase change and interferes as the image wave in the imaging plane. It is important to realize that the recorded image is not a direct representation of the samples crystallographic structure.

Applications:

Because of its high resolution, it is an invaluable tool to study nanoscale properties of crystalline material. At present, the highest resolution possible is 0.8 A. At these small scales, individual atoms and crystalline defects can be imaged.

2.4.1.1.5 Atomic Force Microscope (AFM)

The atomic force microscope is ideal for quantitatively measuring the nanometer scale surface roughness and for visualizing the surface nano-texture on many types of material surfaces including polymer nanocomposites and nanofinished or nanocoated textiles. Advantages of the AFM for such applications are derived from the fact that the AFM is nondestructive technique and it has a very high three dimensional spatial resolution.

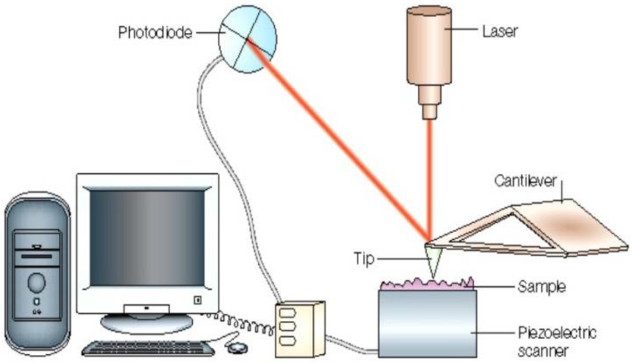


Figure 2.10 Schematic representation of the components of an atomic force microscope

Basic Principle:

The basic principle and applications of atomic force microscopy have been the subject of a number of excellent reviews as reported by Rynders et al., 1995; Wei & Wang, 2004; Poletti et al., 2003 [108-110]. In atomic force microscopy, a probe consisting of a sharp tip (nominal tip radius is in the order of 10 nm) located near the end of a cantilever beam is raster scanned across the surface of a specimen using piezoelectric scanners. Changes in the tip specimen interaction are often monitored using an optical lever detection system, in which a laser is reflected off of the cantilever and onto a position-sensitive photodiode. During scanning, a particular operating parameter is maintained at a constant level, and images are generated through a feedback loop between the optical detection system and the piezoelectric scanners. There are three scan modes for AFM, namely contact mode, non contact mode and tapping mode. In contact mode, the tip scans the specimen in close contact with the surface of the material. The repulsive force on the tip is set by pushing the cantilever against the specimen's surface with a piezoelectric positioning element. The deflection of the cantilever is measured and the AFM images are created. In non-contact mode, the scanning tip hovers about 50-150 A above the specimen's surface. The attractive forces acting between the tip and the specimen are measured, and topographic images are constructed by scanning the tip above the surface. Tapping mode imaging is implemented in ambient air by oscillating the cantilever assembly at its resonant frequency (often hundreds of kilohertz) using a piezoelectric crystal. The piezo motion causes the cantilever to oscillate when the tip is not in contact with the surface of a material. The oscillating tip is then moved towards the surface until it begins to tap the surface. During scanning, the vertically oscillating tip alternately contacts the surface and lifts off, generally at a frequency of 50,000-500,000 cycles/s. As the oscillating cantilever begins to intermittently contact the surface, the cantilever oscillation is reduced due to energy loss caused by the tip contacting the surface. The reduction in oscillation amplitude is used to measure the surface characteristics.

Applications:

The use of this new tool is of importance in fundamental and practical research and development of versatile technical textiles for a variety of applications. Atomic force microscopy can be used to explore the nanostructures, properties, and surfaces and interfaces of fibres and fabrics. For example, structural characteristics of nanofibre materials, nanolevel surface modification of textile surfaces (by plasma or LTV eximer lamp, etc) can be easily assessed by this sophisticated technique. AFM provides powerful tools for nondestructive characterization of textiles. A possible way to investigate the effect of processing on the morphology of the textile surfaces is given by AFM as reported by Sakurai et al. in 2007 [111]. Changes in the morphology of surface modified textile samples can also be quantified by root-mean-square (rms) surface roughness and surface area values.

2.4.1.1.6 Scanning Tunneling Microscopy (STM)

Scanning tunneling microscopy is an instrument for producing surface images with atomic-scale lateral resolution, in which a fine probe tip is scanned over the surface of a conducting specimen, with the help of a piezoelectric crystal at a distance of 0.5-1 nm. and the resulting tunneling current or the position of the tip required to maintain a constant tunneling current is monitored.

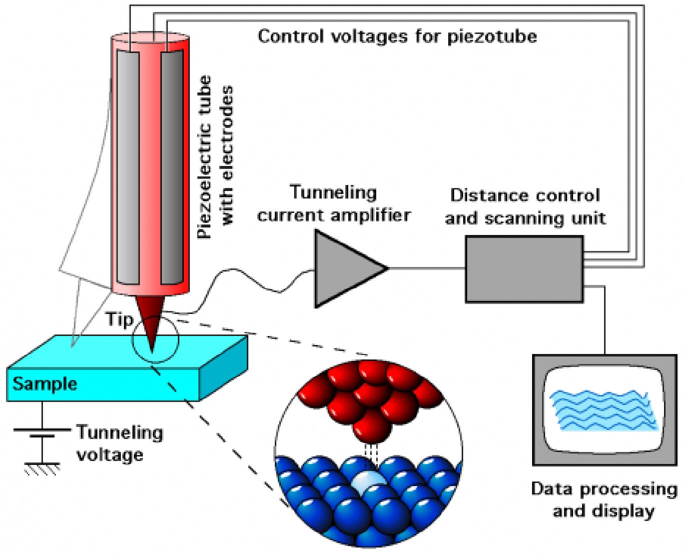


Figure 2.11 A schematic view of a scanning tunneling microscope (STM).

Source: http:// www.answers.com/topic/scanning-tunneling-microscope [112].

Basic Principle:

The principle of STM is based on the concept of quantum tunneling. When a conducting tip is brought very near to a metallic or semi-conducting surface, a bias between the two can allow electrons to tunnel through the vacuum between them F or low voltages, this tunneling current is a function of the local density of states at the Fermi level of the sample. Variations in current as the probe passes over the surface are translated into an image. For STM, good resolution is considered to be 0.1 nm lateral resolutions and 0.01 nm depth resolutions. They normally generate images by holding the current between the tip of the electrode and the specimen at some constant value by using a piezoelectric crystal to adjust the distance between the tip and the specimen surface, while the tip is piezoelectrically scanned in a raster pattern over the region of specimen surface being imaged by holding the force, rather than the electric current, between tip and specimen at a set-point value. Atomic force microscopes similarly allow the exploration of nonconducting specimens. In either case, when the height of the tip is plotted as a function of its lateral position over the specimen, an image that looks very much like the surface topography results. The STM can be used not only in ultra high vacuum but also in air and various other liquid or gas, at ambient and wide range of temperatures. STM can be challenging technique, as it requires extremely clean surfaces and sharp tips.

Applications:

Scanning tunneling microscopy is a powerful tool in nanotechnology and nanoscience providing facilities for characterization and modification of a variety of materials. STM is successfully used to detect and characterize materials like carbon nanotubes (single-walled and multi-walled) and graphine layer. The instrument has also been used to move single nanotubes or metal atoms and molecules on smooth surfaces with high precision as reported by Terrones et al., 2004; Meier et al., 2004 [113, 114].

2.4.1.2 Analysis by spectroscopy

2.4.1.2.1 Infrared spectroscopy

Infrared spectroscopy is one of the most powerful analytical techniques, which offers the possibility of chemical identification. This technique when coupled with intensity measurements may be used for quantitative analysis. One of the important advantages of infrared spectroscopy over the other usual methods of structural analysis (X-ray diffraction, electron spin resonance, etc.) is that it provides information about the structure of a molecule quickly, without tiresome evaluation methods. This technique is based upon the simple fact that a chemical substance shows marked selective absorption in the infrared region giving rise to close-packed absorption bands called an IR absorption spectrum, over a wide wavelength range. Various bands will be present in the IR spectrum, which will correspond to the characteristic functional groups and bonds present in a chemical substance. Thus an IR spectrum of a chemical substance is a fingerprint for its identification. IR spectrum of polymer nanocomposite shows the presence of both nanomaterials and polymers (depending upon the polymer chain) at various frequencies [115].

Fourier Transform Infrared Spectroscopy (FTIR):

Fourier Transform Infrared Spectroscopy, more commonly referred to as a FTIR, is one of the most important technique to characterize polymer, fibre, film and composite. The term Fourier Transform Infrared Spectroscopy (FTIR) refers to a fairly recent development in the manner in which the data is collected and converted from an interference pattern to a spectrum. Applications of the technique cover the whole spectrum from simple material identification to the distribution of materials to their interactions. Today's FTIR instruments are computerized which makes them faster and more sensitive than the older dispersive instruments [116]. The instruments are relatively easy to use; the interpretation of results is usually simple. Sampling techniques allow for non invasive analysis. Relatively small analysis time allow for a rapid analysis of sample or analysis of a large number of samples.

Physical Principles:

Molecular bonds vibrate at various frequencies depending on the elements and the type of bonds. For any given bond, there are several specific frequencies at which it can vibrate. According to quantum mechanics, these frequencies correspond to the ground state (lowest frequency) and several excited states (higher frequencies). One way to cause the frequency of a molecular vibration to increase is to excite the bond by having it absorb light energy. For any given transition between two states the light energy (determined by the wavelength) must exactly equal the difference in the energy between the two states [usually ground state (E_0) and the first excited state (E_1)].

Difference in Energy Levels = Energy of Light Absorbed

$$\mathbf{E_1 - E_2 = h\ c / \lambda} \quad \text{- - - - - - - - - - - - - - - - Equation 2.2}$$

The energy corresponding to these transitions between molecular vibrational states is generally 1-10 kilocalories/mole which corresponds to the infrared portion of the electromagnetic spectrum [116].

Working

A Fourier Transform Infrared (FTIR) spectrometer obtains infrared spectra by first collecting an interferogram of a sample signal with an interferometer, which measures all of infrared frequencies simultaneously. An FTIR spectrometer acquires and digitizes the interferogram, performs the FT function, and outputs the spectrum.

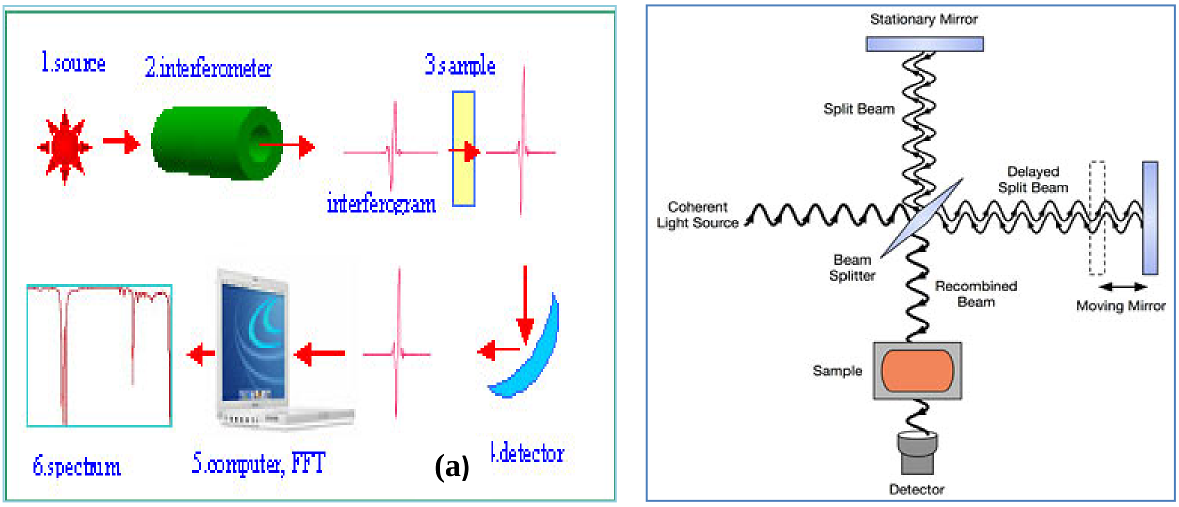


Figure 2.12 (a) Schematic illustration of FTIR [117]; (b) Michelson interferometer, configured for FTIR [118].

The Sample Analysis Process:

The normal instrumental process is as follows:

1. The Source: Infrared energy is emitted from a glowing black-body source. This beam passes through an aperture which controls the amount of energy presented to the sample (and, ultimately, to the detector).
2. The Interferometer: The beam enters the interferometer where the “spectral encoding” takes place. The resulting interferogram signal then exits the interferometer.
3. The Sample: The beam enters the sample compartment where it is transmitted through or reflected off of the surface of the sample, depending on the type of analysis being accomplished. This is where specific frequencies of energy, which are uniquely characteristic of the sample, are absorbed.
4. The Detector: The beam finally passes to the detector for final measurement. The detectors used are specially designed to measure the special interferogram signal.
5. The Computer: The measured signal is digitized and sent to the computer where the Fourier transformation takes place. The final infrared spectrum is then presented to the user for interpretation and any further manipulation [119].

Michelson interferometer:

The main part of a FTIR is Michelson interferometer. An interferometer utilizes a beam splitter to split the incoming infrared beam into two optical beams. One beam reflects off of a flat mirror which is fixed in place. Another beam reflects off of a flat mirror which travels a very short distance (typically a few millimetres) away from the beam-splitter. The two beams reflect off of their respective mirrors and are recombined when they meet together at the beam-splitter. The re-combined signal results from the “interfering” with each other. Consequently, the resulting signal is called interferogram, which has every infrared frequency “encoded” into it. When the interferogram signal is transmitted through or reflected off of the sample surface, the specific frequencies of energy are adsorbed by the sample due to the excited vibration of function groups in molecules. The infrared signal after interaction with the sample is uniquely characteristic of the sample. The beam finally arrives at the detector and is measure by the detector. The detected interferogram cannot be directly interpreted. It has to be “decoded” with a well-known mathematical technique in term of Fourier Transformation. The computer can perform the Fourier transformation calculation and present an infrared spectrum, which plots adsorbance (or transmittance) versus wavenumber [117]**.**

Advantages:

- Much easier to mount and measure samples.
- Can work with solids, liquids, gases.
- Is easier to vary other sample properties.

Application Areas:

- Qualitative analysis – where the aim is to identify the samples.
- Quantitative analysis – where the intensity of absorption is related to the concentration of the component.
- Chemical analysis
- Match spectra to known databases, identifying an unknown samples, forensics
- Monitor chemical reaction in-situ.
- Structural analysis
- Measure optical conductivity – determine if metal, insulator, superconductor, semi conductor.

2.4.1.2.2 Raman Spectroscopy

Raman spectroscopy is a spectroscopic technique used in condensed matter physics and chemistry to study vibrational, rotational, and other low-frequency modes in a system. It relies on inelastic scattering, or Raman scattering of monochromatic laser light. The laser light interacts with phonons or other excitations in the system resulting in the energy of the laser photons being shifted up or down. The shift in energy gives information about the phonon modes in the system.

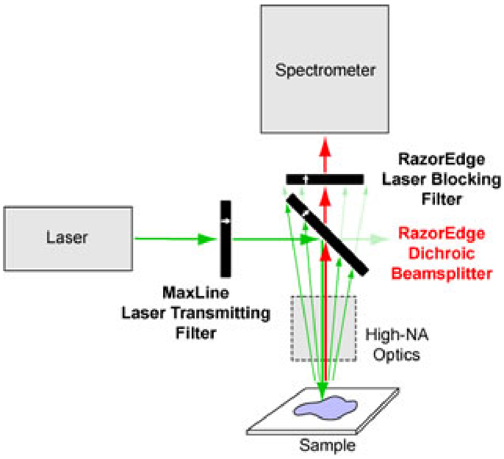


Figure 2.13 A schematic of Raman spectroscopy

Basic Principle:

The Raman Effect occurs when light impinges upon a molecule interacts with the electron cloud of the bonds of that molecule and incident photon excites one of the electrons into a virtual state. For the spontaneous Raman Effect, the molecule will be excited from the ground state to a virtual energy state, and relax into a vibrational excited state, which generates stokes Raman scattering. If the molecule was already in an elevated vibrational energy state, the Raman scattering is then called anti-stokes Raman scattering. A molecular polarizability change or amount of deformation of the electron cloud, with respect to the vibrational coordinate is required for the molecule to exhibit the Raman Effect. The amount of the polarizability change will determine the Raman scattering intensity, whereas the Raman shift is equal to the vibrational level that is involved.

Applications:

Raman spectroscopy is commonly used in chemistry, since vibrational information is very specific for the chemical bonds in molecules. It therefore provides a fingerprint by which the molecule can be identified in the range of 500-2000 cm1. Raman gas analyzers have many practical applications. For instance, they are used in medicine for real-time monitoring of an aesthetic and respiratory gas mixture during surgery. In solid state physics, spontaneous Raman spectroscopy is used to characterize materials, measure temperature, and find the crystallographic orientation of a sample. The polarization of the Raman scattered light with respect to the crystal and the polarization of the laser light can be used to find the orientation of the crystal. As stated by Gouadec & Colomban, 2007 [120].

Raman active fibres, such as aramid and carbon, have vibrational modes that show a shift in Raman frequency with applied stress. Polypropylene fibres also exhibit similar shifts. The radial breathing mode is a commonly used technique to evaluate the diameter of carbon nanotubes. As reported by Eitan et al., 2007 [121].

2.4.1.2.3 Ultraviolet-Visible (UV-VIS) Spectroscopy

Ultraviolet spectrophotometers consist of a light source, reference and sample beams, a monochromator and a detector. The ultraviolet spectrum for a compound is obtained by exposing a sample of the compound to ultraviolet light from a light source, such as a Xenon lamp.

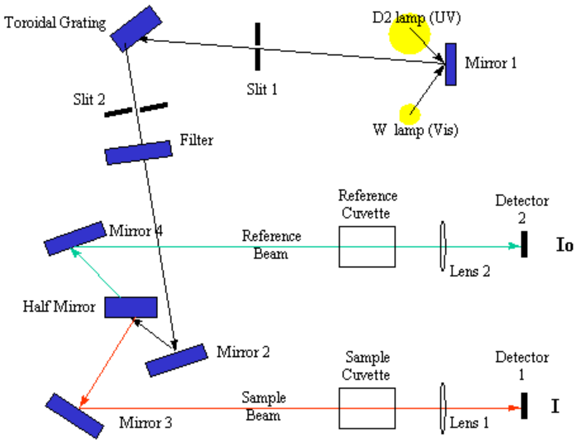


Figure 2.14 A schematic of Ultraviolet-Visible (UV-VIS) Spectroscopy

Basic Principle:

The reference beam in the spectrophotometer travels from the light source to the detector without interacting with the sample. The sample beam interacts with the sample exposing it to ultraviolet light of continuously changing wavelength. When the emitted wavelength corresponds to the energy level which promotes an electron to a higher molecular orbital, energy is absorbed. The detector records the ratio between reference and sample beam intensities (MI). The computer determines at what wavelength the sample absorbed a large amount of ultraviolet light by scanning for the largest gap between the two beams. When a large gap between intensities is found, where the sample beam intensity is significantly weaker than the reference beam, the computer plots this wavelength as having the highest ultraviolet light absorbance when it prepares the ultraviolet absorbance spectrum, as per reported on website http:// www.science of spectroscopy.info/edit/index.php [122].

Applications:

In certain metals, such as silver and gold, it has been found by Patakfalvi, Oszko & De'ka'iiy in 2003; Pal, Tak & Song in 2007; Mock et al. in 2002 [123-125] that, the plasmon resonance is responsible for their unique and remarkable optical phenomena. Metallic (silver or gold) nano-particles, typically 40-100 nm in diameter, scatter optical light elastically with remarkable efficiency because of a collective resonance of the conduction electrons in the metal known as surface plasmon resonance. The surface plasmon resonance peak in UV absorption spectra is shown by these plasmon resonant nano-particles. The magnitude, peak wavelength, and spectral bandwidth of the plasmon resonance associated with a nano-particle are dependent on the particle's size, shape, and material composition, as well as the local environment.

Besides biological labeling and nanoscale biosensing silver nano-particles have received considerable attention to the textile and polymer researchers due to their attractive antimicrobial properties. The surface plasmon resonance peak in absorption spectra of silver particles is shown by an absorption maximum at 420-500 nm. The surface peaks vary with size, shape and concentration of the metallic nano-particles. This shape of the nano-particles can be identified by observing the corresponding peak as reported by Brause, Moeltgen & Kleinermanns, 2002; MuLvaiiey, 1996; Mie, [126-128].

2.4.1.3 Analysis by X-rays

2.4.1.3.1 Wide Angle X-Ray Diffraction

X-ray diffraction has played a central role in identifying and characterizing solids since a long period of time. The nature of bonding and the working criteria for distinguishing between short-range and long-range order of crystalline arrangements from the amorphous substances are largely derived from X-ray diffraction and thus it remains as a useful tool to obtain structural information. X-ray diffraction pattern of amorphous polymer will not show any sharp and highly intensed peaks whereas the nanocomposites of amorphous polymer show sharp and highly intensed peaks. This is due to the development of crystallinity in the amorphous polymer. In order to obtain detailed structural information, knowledge of X-ray diffraction intensities is also essential, the intensities being related to the structure factor [115].

X-rays are electromagnetic radiation similar to light, but with a much shorter wavelength (few Angstrom). They are produced when electrically charged particles of sufficient energy are decelerated. In an X-ray tube, the high voltage maintained across the electrodes draws electrons toward a metal target (the anode). X-rays are produced at the point of impact, and radiate in all directions.

Basic Principle:

If an incident X-ray beam encounters a crystal lattice, general scattering occurs. Although most scattering interferes with itself and is eliminated (destructive interference), diffraction occurs when scattering in a certain direction is in phase with scattered rays from other atomic planes. Under this condition the reflections combine to form new enhanced wave fronts that mutually reinforce each other (constructive interference). The relation by which diffraction occurs is known as the Bragg's law or equation as per Sosa, Noguez & Barrera, 2003 [129]. As each crystalline material including the semi crystalline polymers as well as metal and metal oxide nano-particles and layered silicate nanoclays have a characteristic atomic structure, it will diffract X-rays in a unique characteristic diffraction order or pattern.

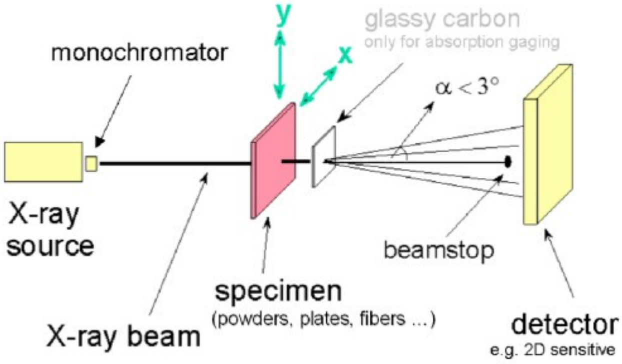


Figure 2.15 Schematic of Wide Angle X-Ray Diffraction

Applications:

X-ray diffraction data from polymers generally provide information about crystallinity, crystallite size, orientation of the crystallites and phase composition in semi crystalline polymers. With appropriate accessories, X-ray diffraction instrumentation can be used to study the phase change as a function of stress or temperature, to determine lattice strain, to measure the crystalline modulus, and with the aid of molecular modeling to determine the structure of polymer.

Besides the above mentioned characterization this sophisticated technique can also be used to characterize polymer layered silicate (clay), silicate nanoclay interest both in characterize polymer layered nanocomposites, Polymer/layered composites have attracted great industry and in academia, because they often exhibit remarkable improvement in materials properties at very low clay content (3-6 wt %), when compared with virgin polymer or conventional composites. The use of organoclays as precursors to nanocomposite formation has been extended into various polymer systems (thermoset and thermoplastic) including epoxy and others.

For true nanocomposites, the clay nanolayers must be uniformly dispersed and exfoliated in the polymermatrix. The structure of polymer/layered silicates composites has typically been established using wide angle X-ray diffraction (WAXD) analysis. By monitoring the position, shape and intensity of the basal reflections from the distributed silicate layers, the nanocomposite structure (intercalated or exfoliated) may be identified. In an exfoliated nanocomposite, the extensive layer separation associated with the delamination of the original silicate layers in the polymer matrix results in the eventual disappearance of any coherent X-ray diffraction from the distributed silicate layers. On the other hand Ray & Okamota in 2003 [8], for intercalated nanocomposites, the finite layer expansion associated with the polymer intercalation results in the appearance of a new basal reflection corresponding to the larger gallery height. Organophilic clay (also known as nanoclay) can be obtained by simply the ion-exchange reaction of hydrophilic clay with an organic cation such as an alkyl ammonium or phosphonium ion to make it compatible with polymeric matrix. The inorganic ions, relatively small (sodium), are exchanged with more voluminous organic onium cations as per Lagaly G [130]. This ion-exchange reaction results in widening the gap between the single sheets, enabling organic cations chain to move in between them. This increase in d-space or degree of exfoliation of the polymer nanocomposite can be obtained from Bragg equation. The X-ray diffractograms by Patel et al. in 2006 [131] of the organoclay reveals a shift in the position of [001] planes (26 changed from 5-7° to 4-32°), indicating an increase in the basal spacing of these planes. The increase is relatively large from 1-5 nm to 2 06 nm and confirms the occurrence of organic molecule intercalation between silicate platelets.

2.4.1.3.2 X-Ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy is a quantitative spectroscopic surface chemical analysis technique used to estimate the empirical formula or elemental composition, chemical state and electronic state of the elements on the surface (up to 10 nm) of a material. XPS is also known as ESC A, an abbreviation of electron spectroscopy of chemical analysis.

Basic Principle:

X-ray irradiation of a material under ultra-high vacuum (UHV) leads to the emission of electrons from the core orbital of the top 10 nm of the surface elements of the material being analyzed. Measurement of the kinetic energy (KE) and the number of electrons escaping from the surface of the XPS material gives the XPS spectra. From the kinetic energy, the binding energy of the electrons to the surface atoms can be calculated. The binding energy of the electrons reflects the oxidation state of the specific surface elements. The number of electrons reflects the proportion of the specific elements on the surface.

As the energy of a particular X-ray wavelength used to excite the electron from a core orbital is a known quantity, to determine the electron binding energy (BE) of each of the emitted electrons by using the following equation that is based on the work of Ernest Rutherford (1914):

$$E_{\text{binding}} = E_{\text{photon}} - E_{\text{kinetic}} - \Phi \qquad \text{………………..Equation 2.3}$$

Where, E_{binding} is the energy of the electron emitted from one electron configuration within the atom; E_{photon}, the energy of the X-ray photons being used; E_{kinetic}, the kinetic energy of the emitted electron as measured by the instrument; and 0, the work function of the spectrometer (not the material) (Crist, 2005) [132].

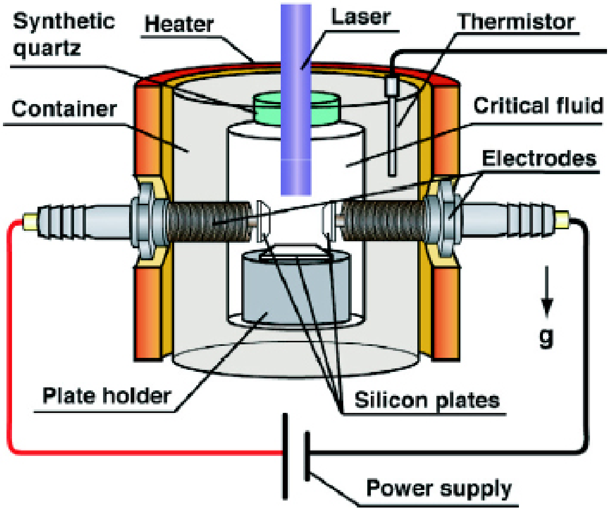


Figure 2.16 Schematic view of X-Ray Photoelectron Spectroscopy

Applications:

XPS is used to determine the elements and the quantity of those elements that are present within -10 nm of the sample surface. It also detects the contamination, if any, exists in the surface or the bulk of the sample. If the material is free of excessive surface contamination, XPS can generate empirical formula of the sample and the chemical state of one or more of the elements can be identified. Moreover, the technique can be used to determine the thickness of one or more thin layers (1-8 nm) of different materials within the top 10 nm of the surface. It can also measure the uniformity of elemental composition of textile surfaces after nanolevel etching, finishing or coating of the surfaces. The only limitation is that it cannot detect hydrogen (Z=l) or helium (Z=2), because these two elements do not have any core electron orbitals, but only valence orbitals.

2.4.2 Thermal analysis

2.4.2.1 Thermo gravimetric analysis (TGA)

TGA measures the amount and rate of change in the mass of a sample as a function of temperature or time in a controlled atmosphere. The measurements are used primarily to determine the thermal and/or oxidative stabilities of materials as well as their compositional properties. The technique can analyze materials that exhibit either mass loss or gain due to decomposition, oxidation or loss of volatiles (such as moisture). It is especially useful for the study of polymeric materials, including thermoplastics, thermosets, elastomers, composites, films, fibres, coatings and paints.

The technique is particularly useful for the following types of measurements:

- Compositional analysis of multi-component materials or blends
- Thermal stabilities
- Oxidative stabilities
- Estimation of product lifetimes
- Decomposition kinetics
- Effects of reactive atmospheres on materials
- Filler content of materials
- Moisture and volatiles content [133].

2.4.2.2 Differential scanning calorimetry (DSC) and Differential thermal analysis (DTA)

Differential thermal analysis (DTA) is a technique in which the temperature difference between a substance and a reference material is measured as a function of temperature while the substance and reference material are subjected to a controlled temperature program.

In DSC, the difference in energy inputs into a substance and a reference material is measured as a function of temperature while the substance and reference material are subjected to a controlled temperature program.

Based on the method of measurement, DSC is of two types:

1. Power compensation differential scanning calorimetry (power compensation DSC).

2. Heat-flux differential scanning calorimetry (heat-flux DSC).

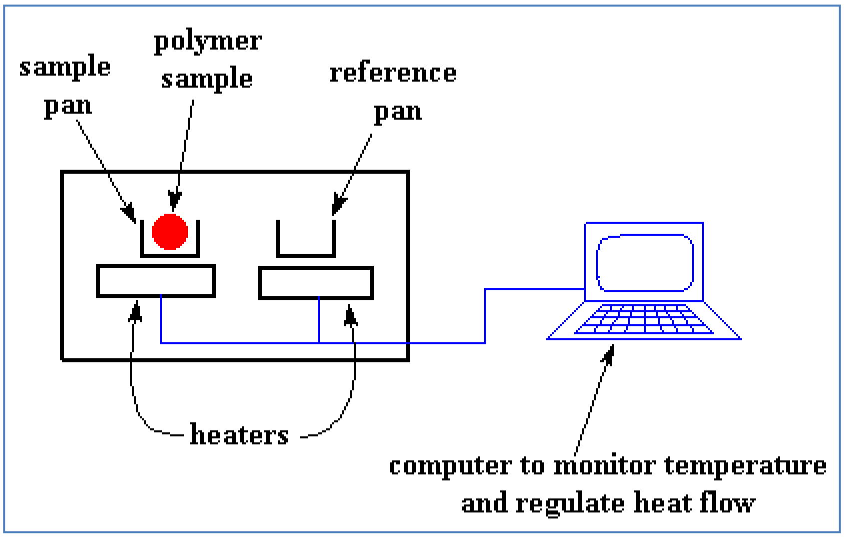


Figure 2.17 Schematic diagram of DSC/DTA

In DSC, the given sample and the reference material are kept in separate crucibles in the same furnace which is heated at programmed heating rate. There is an extra heater provided just below the crucible carrying the sample, which operates on the instructions received from the device measuring the temperature difference (ΔT) between the sample and the reference, to maintain the ΔT as zero. Thus the DSC trace records the extra (ΔH) supplied per unit time to the sample crucible as a function of the overall temperature of the furnace.

The principal use of DSC/DTA is the measurement of transition temperature, the measurement of transition enthalpy, and the measurement of heat capacity. Transition temperature is determined as extrapolated onset temperature, and transition enthalpy is determined by integration of the signal with special methods used for the glass transition.

The simplest use of DSC/DTA is in identification and characterization of materials. Identification process involves determination of sample transition temperature and/or transition enthalpy for an unknown sample, followed by a comparison with a list of possible materials with their transition temperatures and/or enthalpies. Characterization involves the determination of transition temperature and/or enthalpy for a known sample.

Modulated DSC (MDSC) is a relatively new technique that improves upon the classical DSC performance in terms of increased ability to analyze complex transitions, higher sensitivity, and higher resolution.

2.5 PRESENT STATUS OF RESEARCH IN POLYMER NANOCOMPOSITE MATERIALS

Metal oxides enhance the mechanical properties of the polymer composites [134]. Generally tensile properties such as strength, elastic modulus, work, stiffness, stress-at-break increase while elongation at break decreases [135, 136]. Researchers have reported that the elastic modulus of nanocomposites increases as the size of the reinforcement is reduced, provided that there was a good interaction between the filler and the polymer matrix. For some nanocomposites with very small reinforcement particles, young's modulus is greater than might be expected from the volume law of mixtures of the constituents and this is attributed to the modification to the structure of the matrix surrounding the nanoparticles due to their high surface area.

For polymer systems where a high degree of crystallinity is possible, the increase in modulus with a reduction in particle size is found to be even greater unless there is poor interaction between filler and matrix. The modulus increases with the volume fraction of the reinforcement as expected until aggregation of the particles occurs when the modulus can be reduced in some systems. The yield strength of a polymer nanocomposite is critically dependent on the interaction between the reinforcement and the matrix. Where this interaction is strong the yield stress tends to increase with increasing volume fraction of reinforcement and decreasing particle size. This changes when there is poor interaction where an increase in volume fraction leads to a yield stress decrease from the value for the unreinforced matrix, regardless of the filler concentration or size. The ultimate tensile strength follows a similar pattern to the yield stress. Thus, to achieve nanocomposites with good mechanical properties it is critical that the matrix–reinforcement interfacial chemistry is controlled to give strong adhesion.

As the stiffness of the nanocomposite increases, so, in general, does its strength and this is accompanied by a reduction in its strain to failure [135, 136]. The strain to failure for a nanocomposite material is often higher than when the reinforcement is micrometre-sized. However, there are exceptions to this and, as with strength, it critically depends on the bonding between the reinforcement and the matrix – if this is poor then both the stress and strain to failure are reduced. Also the dispersion of nano material should be uniform to increase the interaction between the reinforcement and the matrix. On the other hand, nano particles may agglomerate and thus degrade the properties of the nano composites [134]. Due to loading of silica nano particles, there is increase in tensile strength, elasticity or fiber stiffness collectively stated by Hagenmueller, et al., 2003; Poncharal, et al., 1999; Stegmaier, 2006; Kalarikkal, Sankar, and Ifju, 2006 [12-15]. These properties can lead to the production of stronger or more elastic textiles or increase the wear and tear resistance of a fabric. Mahltig, Haufe, and Bottcher, 2005 [22] further reports the possibility to increase the abrasion stability of polyester by treating the finished fabric with a SiO_2 coating. The coating is produced through a sol-gel process which involves the production of a nanoparticulate SiO_2 dispersion.

Nano particles are added to composite materials to improve their viscoelastic properties. The heat distortion temperature for nanocomposites tends to be higher than that of the unfilled matrix or microreinforced materials because of an increase in viscosity during composite manufacture and a reduction in viscous deformation afterwards. The increase in tensile strength or young's modulus for nanocomposites compared with microcomposites can partly be explained by the details of the interaction between the filler and the matrix. Good adhesion between matrix and particle results in less de-bonding when a stress is applied and consequently the strength is improved. The polymer in the proximity of a particle to which there is good adhesion tends to have higher density which also results in an increase in stiffness [137]. The polymer adjacent to this high-density region will have a lower density as the chains are moved towards the particle to make the high-density region. For large particles this lower density region will be relatively large and the contribution of the high modulus filler will be diminished compared with the case when the filler particle is small.

For nanocomposites, the number of particles for a given volume fraction is much larger and the particles will be much closer to each other. If the reinforcement particles are very densely packed then the high density boundary layer will make up a larger proportion of the matrix and the modulus will increase. Thus, the major improvements to the mechanical properties of nanocomposites arise from the small particle spacing, rather than directly from the size or volume fraction of the reinforcement particles used.

Table 2.1 Nano materials and techniques to enhance mechanical properties of textiles

NP/ Nanostructure	Textile material	Production method	Integration into the textile matrix
SiO_2	polyester	coating of finished fabric by sol-gel process	Nanoporous SiO_2 coating as a crosslinked network
CNT	PVA	Co-flowing stream of CNT-dispersion during solution spinning	No information
	PVA	modified solution spinning process of CNT dispersion	PVA coated CNT
	PS, PP	melt compounding and subsequent melt spinning	PS CNT composite
	not specified	dip or spray coating of finished textile	Network of CNT clusters on fibre surface
ZnO	Cotton	coating of finished fabric by dip pad dry cure method	ZnO NP coating
Al_2O_3	not specified	dip coating of finished fabric	Single Al_2O_3 particles on the surface
Polybutylacrylate (PBA)- NP1)	not specified	production of PBA/PS nanocomposite by two stage solution polymerization; dip coating of the finished fabric with aqueous dispersion of the obtained composite	PBA/PS nanocomposite coating

Apart from CNT, also other NP were reported to alter or improve the mechanical properties of the textile fibers. The appliance of a ZnO nanoparticle based coating was observed to increase the stiffness of a fabric. The coating was thereby applied by dipping the fabric into a nanodispersive ZnO solution and a subsequent dry-pad-cure process by Yadav, et al., 2005 [20]. Kalarikkal, Sankar, and Lfju, 2006 [15] used a similar process to provide different textile materials with a nanoparticulate Al_2O_3 coating which led to an increase in fracture toughness. To optimize the mechanical properties of carpet backings, Campos, et al., 2006 [21] used a PS - composite containing polybutylacrylate (PBA)-NP as coating.

Nanoengineering can be used to produce fibers that act as carriers for drugs, fragrances or other active agents and enable the controlled release of the incorporated species. Research projects with the aim to produce antibacterial fabrics through the controlled release of a biocidal agent Persico, Carfagna, and Musto, 2006 [159] used a montmorillonite-nanoclay as carrier for cosmetic jojoba oil substances to produce nylon fibers which could find applications in skin care products. The jojoba oil and nanoclays were incorporated into the polyamid-matrix by direct melt compounding. Mahltig, Haufe, and Bottcher, 2005 [22] report the possibility of producing fibers with controlled release of different agents (e.g. drugs, ethereal oils, or insect repelling fragrances) by including them into a SiO_2-Nanosol coating.

2.6 POSSIBLE APPLICATIONS

Reinforced fibers could find applications in the apparel industry, the fabrication of upholstery, in geotextiles Lubben, 2005 [23], industrial textiles or the production of protective clothing by Mahltig, Haufe, and Bottcher, 2005 [22]. In the apparel industry and upholstery sector, such fibers might be used to produce wear and tear resistant clothes or furniture textiles. Their application in the production of protective clothing could furthermore lead to the development of stronger and more lightweight safety harnesses and bullet proof vests, Ward,2003 [24]. In a lightweight military battle suit which is able to withstand blasts and which is currently under development, reinforced fibers would fulfill a similar function as web.mit.edu [25]. Nano-reinforced fibers could also be used to produce stronger and more durable Geotextiles which are used in the construction sector for sealing, isolation or erosion control by Lubben, 2005 [23]. In industrial textiles, the nano-reinforced fibers could find applications in filters or sieves with improved abrasion stability, as they are used in paper production as per Mahltig, Haufe, and Bottcher, 2005 [22]. The film produced from PA can possibly be applied in the area such as food packaging industry. PA is a widely used material for the production of flexible packaging film, in most cases combined with polyolefins as a component of a multilayer structure. It has found numerous applications for its unique combination of properties like mechanical strength, transparency, thermoformability and barrier [160].

Available products:

In the conducted Internet research, the following two commercially available products could be found: CNT-reinforced fibers for antiballistic purposes (e.g. bullet proof vests or doors) US global Nanospace, 2007 [26] and CNT containing polymer additives for the production of reinforced textiles Zyvexpro Materials, 2007 [27].

BASF is producing high quality flexible film for packaging of oxygen sensitive food such as ham, cheese, processed food and sausage from polyamide film under the trade name Ultramid®. This product is also well suited for the production of biaxially oriented (BOPA) film which provides high stiffness, puncture resistance, barrier and transparency. Polyamide sausage casing is characterized by a high oxygen barrier as well as good printing properties and gauge consistency [161].

2.7 OBJECTIVES

Now a day's research has concentrated on preparation of polymer /nano composite materials with high modulus, increased strength and heat resistance. Improvement in mechanical properties of the new composite materials is depending on proper selection of polymer and nano particles to be incorporated within its matrix. Recently many researchers have carried out more experiments concerning the combination of polymer and nanoparticles [160-165]. Another concern in research and development of composite materials is the different techniques used to engineer the structure of these nanocomposites with improved properties and probable applications [158, 166-168].

Generally the preparative methods for polymer nanocomposites are divided into three groups based on the starting materials and processing techniques, which were intercalation of polymer or pre-polymer from solution, in situ intercalative polymerization method and melt intercalation method. However, melt intercalation was found to be the most effective way to produce the polymer nanocomposite materials. In recent times this technique has become the standard technique for the preparation of polymer nano composites. This method involves annealing, statically or under shear, and a mixture of the polymer and nanoparticles above the softening point of the polymer. The polymer intercalation structure depends critically on the nanoparticles used and constituent interactions. Significantly this technique has great advantages over either in situ intercalative polymerization or polymer solution interaction. Additionally it is also compatible with current industrial process, such as extrusion and injection moulding. Furthermore, the direct melt intercalation was highly specific for the polymers, leading to new hybrids that were previously inaccessible. Another advantage of this method is an economical method for industries from a waste perspective.

Silica is used primarily in the production of glass for windows, drinking glasses, beverage bottles, and many other uses. The majority of optical fibres for telecommunications are also made from silica. It is a primary raw material for many white-ware ceramics such as earthenware, stoneware and porcelain, as well as industrial portland cement. Silica is a common additive in the production of foods, where it is used primarily as a flow agent in powdered foods, or to absorb water in hygroscopic applications. It is the primary component of diatomaceous earth, which has many uses, ranging from filtration to insect control. It is also the primary component of rice-husk ash, which is used in filtration and cement manufacturing.

Thin films of silica grown on silicon wafers via thermal oxidation methods can be quite beneficial in microelectronics, because of its high chemical stability. In electrical applications, it can protect the silicon, store charge, block current, and even act as a controlled pathway to limit current flow. A silica-based aerogel was used in the Stardust spacecraft to collect extraterrestrial particles. Silica is also used in the extraction of DNA and RNA, due to its ability to bind to the nucleic acids under the presence of chaotropes. As hydrophobic silica, it is used as a defoamer component. In hydrated form, it is used in toothpaste as a hard abrasive to remove tooth plaque. In its capacity as a refractory, it is useful in fibre form as a high-temperature thermal-protection fabric. In cosmetics, it is useful for its light-diffusing properties and natural absorbency. Colloidal silica is used as a wine and juice fining agent. In pharmaceutical products, silica aids powder flow when tablets are formed. Finally, it is used as a thermal-enhancement compound in the ground-source heat-pump industry. Finally it is used in textiles to achieve multi-functional properties to textile composite materials.

Therefore, the interest in using nanosized SiO_2 in the textile industry is increasing. So the purpose of this work is to utilize SiO_2 nanoparticles to prepare high performance polymer-SiO_2 nanocomposite textiles. The present study is therefore focused on the investigation towards application of silica nanoparticles to different forms of polymers i.e. film, filament and fabric with improved mechanical properties compare to the respective material prepared without SiO_2 nanoparticles. Another purpose of the study is to investigate structural transformations occurred due to the incorporation of silica in textile polymeric material in different forms. The structural changes in prepared polymer-silica nanocomposite materials have been analyzed by SEM, EDX, FTIR, XRD and DSC techniques.