



# Nanocomposites – An Overview

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## Abstract

Nano-composites have gained much interest over the past few years. Significant efforts are underway to control the nano-structures via innovative synthetic approaches. The properties of nano-composite materials depend not only on the properties of their individual parents but also on their morphology and interfacial characteristics. By optimized fabrication process and controlled nano-sized dispersion, thermal stability and mechanical properties such as adhesion resistance, flexural strength, toughness & hardness can be enhanced. The paper discusses various forms of nano particles, their structures & characterization along with the fabrication techniques of different nanocomposites using thermoplastics and thermosets as matrices. The possibilities of producing nano materials with tailored physical & electronic properties at low cost could result in interesting applications ranging from drug delivery to corrosion prevention to electronic/automotive parts to industrial equipment and several others. The paper also discusses several current and potential applications of nanocomposites. The cutting edge application delivering chemotherapy drugs in nanoparticle form for reduced side effects by targeting the drugs directly to the tumours merits special mention.

**Keywords** : nano particles, nanocomposites, nanomaterials, nanotubes, exfoliated

## Introduction

Nano-composite is an innovative material having nano (one-billionth of a meter) fillers dispersed in a matrix. Typically, the structure is a matrix-filler combination, where the fillers like particles, fibers, or fragments are surrounded and bound together as discrete units by the matrix. The term nano-composite encompasses a wide range of materials right from three dimensional metal matrix composites to two dimensional lamellar composites and nano-wires of single dimension to zero-dimensional core-shells all representing many variations of mixed & layered materials.

The physical, chemical and biological properties of nano materials differ from the properties of individual atoms and molecules or bulk matter. By creating nano particles, it is possible to control the fundamental properties of materials such as their melting temperature, magnetic properties, charge capacity and even their color without changing the materials' chemical compositions (D.R. Paula L.M.Robeson, 2008, Y.J Liu et.al., 1996).

Nano-particles and nano-layers have very high surface-to-volume and aspect ratios and this makes them ideal for use in polymeric materials. Such structures combine the best properties of each component to possess enhanced mechanical & superconducting properties for advanced applications. The properties of nano-composite materials depend not only on the properties of their individual parents but also on their morphology and interfacial characteristics. Some nanocomposite materials could be 1000 times tougher than the bulk component. The general class of nanocomposite organic/inorganic materials is a fast growing area of research. The inorganic components can be three-dimensional framework systems such as zeolites, two-dimensional layered materials such as clays, metal oxides, metal phosphates, chalcogenides and even one-dimensional and zero-dimensional materials such as  $(\text{Mo}_3\text{Se}_3)_n$  chains and clusters. Thus, nanocomposites promise new applications in many fields such as mechanically reinforced lightweight components, non-linear optics, battery cathodes, nano-wires, sensors and other systems.

Inorganic layered materials exist in many varieties. They possess well defined, ordered intra-lamellar space potentially accessible by foreign species (M.G Kanatzidis et.al, 1990, Y.J. Liu et.al, 1991). This ability enables them to act as matrices for polymers yielding hybrid nanocomposites. Lamellar nano-composites represent an extreme case in which interfacial interactions between two phases are maximized. By engineering the polymer-particle interactions, nano-composites could be produced with a broad range of properties. Lamellar nano-composites can be divided into two distinct classes viz. intercalated and exfoliated. In the former, the polymer chains are alternately present with the inorganic layers in a fixed compositional ratio and have a well-defined number of polymer layers in the intra-lamellar space. In exfoliated nano-composites, the number of polymer chains between the layers is almost continuously variable and the layers stand  $>100 \text{ \AA}$  apart. The intercalated nano-composites are useful for electronic and charge transport properties. On the other hand, exfoliated nano-composites possess superior mechanical properties.

For example, the electronics industry utilizes materials that have high dielectric constants and that are also flexible, easy to process, and strong. Finding single component materials possessing all these properties is difficult. The most commonly used ceramic materials with high dielectric constant are found to be brittle and are processed at high temperatures, while polymeric materials with easy processability have low dielectric constants. Composite materials having micron-scale ferroelectric ceramic particles as the filler in liquid crystal polymer or thermoplastic polymer matrices do not possess ideal processing characteristics and are difficult to form into the thin uniform films used for many microelectronics applications. In such situation, using nano-composite materials is most ideal with a wide range of materials mixed at the nanometer scale.

## What are Nanomaterials?

Nanomaterials have at least one external dimension in the size range

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from approximately 1-100 nanometers and nanoparticles are objects with all three external dimensions at the nanoscale. These nanoparticles are either naturally occurring obtained from volcanic ash, soot from forest fires etc. or they are byproducts of combustion processes (e.g., welding, diesel engines) (Juh Tzeng Lue, 2007, Ghim Wei Ho and Professor Mark Welland, 2009, S. Y Chen et.al, 1987). These materials are physically and chemically heterogeneous and often referred as ultrafine particles. Often, the behavior of nanomaterials may depend more on surface area than particle composition itself. Relative-surface area is one of the principal factors that enhance its reactivity, strength and electrical properties. These nano-scale particles, tubes, rods, or fibres are being used in healthcare, electronics, cosmetics, textiles, information technology and environmental protection. The properties of nanomaterials are not always well-characterized. Important physical and chemical properties of nanomaterials are as follows:

#### 1. Physical properties include:

- Size, shape, specific surface area and ratio of width & height
- Size distribution
- Surface smoothness
- Structure including crystal structure and any crystal defects
- Dissolvability

#### 2. Chemical properties include:

- Molecular structure
- Composition, including purity and known impurities or additives
- State (solid, liquid or gas)
- Surface chemistry
- Attraction to water molecules or oils and fats

Nanomaterials can be metals, ceramics, polymeric materials, or composite materials with a wide range of properties and possible applications. These include extraordinarily tiny electronic devices, miniature batteries to biomedical applications, packaging films, super absorbents, components of armor and parts of automobiles. Nanotechnology can be used to design pharmaceuticals that can target specific organs or cells in the body such as cancer cells and enhance the therapeutic effectiveness. Nanomaterials can also be added to cement, cloth and other materials to make them stronger and yet lighter. Their size makes them extremely useful in electronics and they can also be used in environmental remediation or clean-up by binding with and neutralizing toxins.

Engineered nanoparticles are produced and designed with very specific properties related to shape, size, surface properties and chemistry. These nanoparticles can be produced experimentally by laser ablation, HiPCO (high-pressure carbon monoxide), arc discharge and chemical vapor deposition (CVD) techniques. These materials have unique optical, magnetic, electrical and other properties and have made great impacts in electronics, medicine and other sectors. Engineered nanomaterials include nanocrystals, which are composed of a quantum dot surrounded by semiconductor materials, nano-scale silver, dendrimers (repetitively branched molecules) and fullerenes (carbon molecules in the form of a hollow sphere, ellipsoid or tube).

However, while engineered nanomaterials provide great benefits, their potential effects on human health and the environment are not well known. Nano-sized particles can enter the human body through inhalation and ingestion and through the skin. Fibrous nanomaterials made of carbon have shown to induce inflammation in the lungs similar to asbestos.

#### Nano-Composites – Basic Ingredients

The field of nanotechnology is one of the most important areas for current research and has generated a great deal of interest in polymer nanocomposites over the last few years. Polymer nanocomposites (PNC) consist of a polymer or copolymer (e.g., thermoplastics, thermosets, or elastomers) with nanoparticles or nanofillers dispersed therein. These may be of different shape (e.g., platelets, fibers, spheroids) but at least one dimension must be in the range of 1–50 nm.

Nanoparticles often influence the properties of the composites at very low volume fractions due to their small inter-particle distances and the conversion of a large fraction of the polymer matrix near their surfaces into an interphase of different properties as well as due to the change in morphology (Vikas Mittal, 2009, Di, Y, Iannace et.al, 2003) As a result, the desired properties are usually reached at low filler volume fraction, which allows the nanocomposites to retain the macroscopic homogeneity. Besides, the geometrical shape of the particles plays an important role in determining the properties of the composites. The nanocomposites can contain inorganic fillers falling into three different categories by the virtue of their primary particle dimensions. When all the three dimensions of the particles are in the nanometer scale, the inorganic fillers have spherical shape like silica particles. Fillers with two dimensions in the nanometer scale whereas the third one is in the range of micrometers include carbon nanotubes or whiskers. In case of layered silicate (or alumino-silicate) materials, the filler with two finite dimensions exist in the range of micrometers, whereas the third dimension is in nanometer scale. There are different types of commercially available nano-particles that can be incorporated into the polymer matrix to form polymer nanocomposites. The exact selection of particle is essential to ensure effective penetration of the polymer or its precursor into the interlayer spacing of the reinforcement and result in the desired exfoliated or intercalated product. Polymer could be incorporated either as the polymeric species itself or via the monomer, which is polymerized in situ to give the corresponding polymer based nanocomposite. Most commonly used nano-particles include:

- Montmorillonite organoclays (MMT)
- Carbon nanofibers (CNFs)
- Polyhedral oligomeric silsesquioxane (POSS)
- Carbon nanotubes [multiwall (MWNTs), small-diameter (SDNTs), and single-wall (SWNTs)]
- Nanosilica (N-silica)
- Nanoaluminum oxide (Al<sub>2</sub>O<sub>3</sub>)
- Nanotitanium oxide (TiO<sub>2</sub>)
- Others

Thermosets and thermoplastics used as matrices for making nanocomposites include:

- Nylons
- Polyolefin, e.g. polypropylene
- Polystyrene
- Ethylene-vinyl acetate (EVA) copolymer
- Epoxy resins
- Polyurethanes
- Polyimides
- Poly ethylene terephthalate (PET)

There are two main challenges in developing nanocomposite materials after the desired polymer has been selected for the purpose. First, the choice of nano-particles requires an interfacial interaction and/or compatibility with the polymer matrix. Second, the processing technique should address uniform dispersion and distribution of nano-particles or nano-particle aggregates within the polymer matrix.

In addition, amount of nanoparticulate/fibrous added to polymer matrix also plays significant role in deciding mechanical properties of the nanocomposites. These are generally added in very small quantities to result in improved properties. This in turn could result in significant weight reductions particularly in military and aerospace applications, greater strength and increased barrier performance for similar material thickness, whereas, the micro-dimensional particles/additives require much higher loading levels to achieve similar performance.

There are a few disadvantages that are associated with using nanoparticle viz. toughness and impact performance (B.L Ravi Shankar, May 2009 ,

Unal, H and Mimaroglu, 2004) . Nanoclay modification of polymers such as polyamides could even reduce impact performance. There is a need for better understanding of formulation/structure/property relationships to platelet exfoliation and dispersion etc. The improved properties vis-à-vis the disadvantages of the nano-particles & resultant composites are shown in Table1.

**Processing of Nanocomposites**

Currently practiced processes for forming nanocomposites generally include polymerizing various monomers followed by pelletization of each of the polymers thus formed separately. Nanocomposites can be formed using variety of shear devices, e.g. extruders, mixers, ultrasonicators etc. Polymer layered silicate (PLS) nanocomposites are currently prepared by four different methods (T.D. Fornes & D.R. Paul, 2003)

**In Situ Polymerization**

In this process, the monomers and the filler are mixed and swollen. A molecule (the monomer) is absorbed into a host compound containing inter-planar spaces (channels or cavities) and then polymerized. The polymer thus obtained is called 'intercalated' if confined between layers, or 'occluded' if confined between cavities.

**Solution Process**

Intercalation of the polymer from a solution is a two-stage process in which the polymer is exchanged with an appropriate solvent. There are two immiscible phases present, an aqueous (continuous) phase containing initiator and a non-aqueous (discontinuous) phase containing the monomer or prepolymer. The diminished entropy due to confinement of the polymer is compensated by an increase due to

Table 1: Important Characteristics of Nano-composites

Improved properties	Disadvantages
Mechanical properties (tensile strength, stiffness, toughness)	Viscosity increase (limits processability)
Gas barrier	Dispersion difficulties
Synergistic flame retardant additive	Optical issues
Dimensional stability	Sedimentation
Thermal expansion	Black color when different carbon containing nanoparticles are used
Thermal conductivity	
Ablation resistance	
Chemical resistance	
Reinforcement	

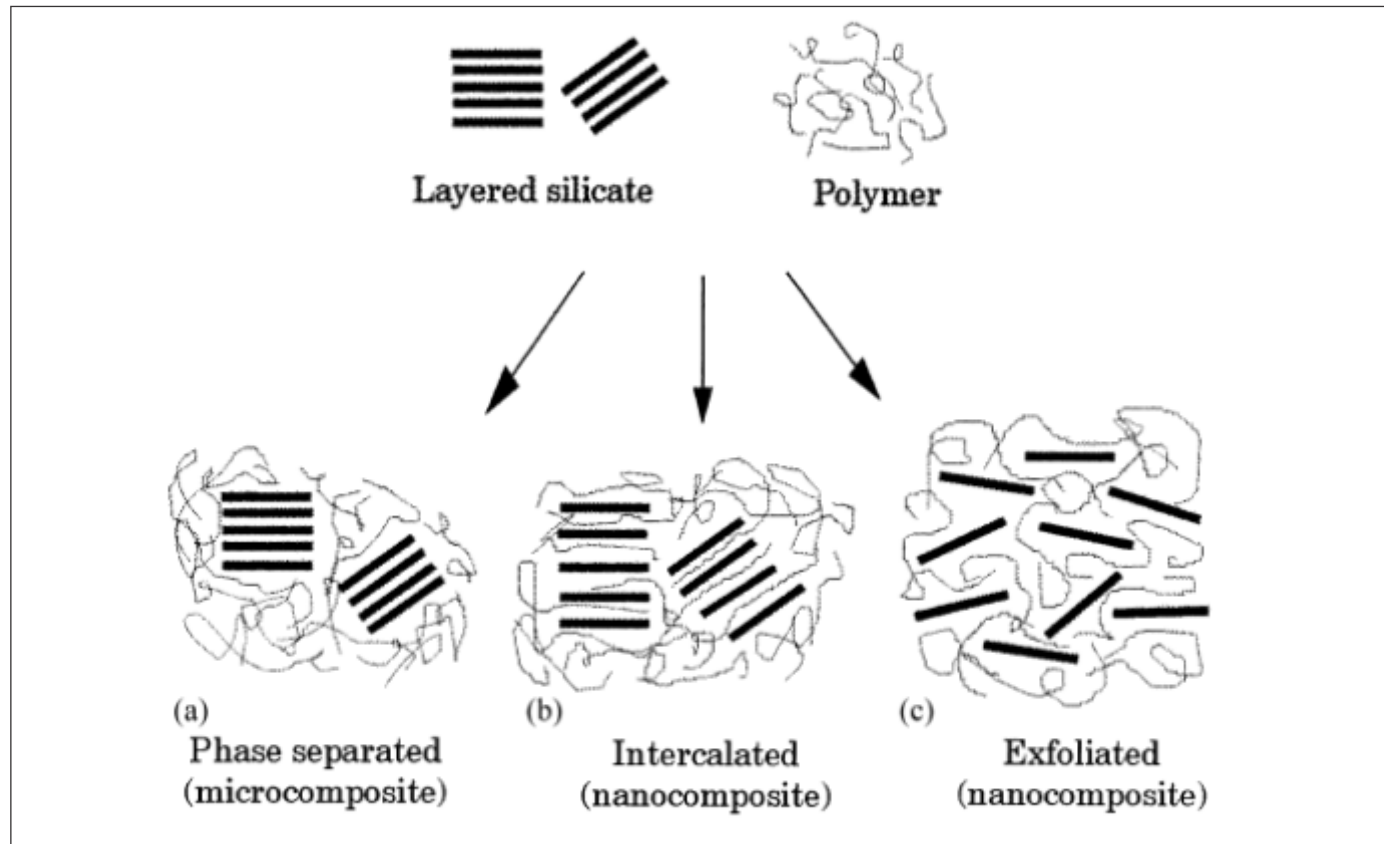


Figure 1. Formation of intercalated and exfoliated nanocomposites from layered silicates and polymers

desorption of intercalated solvent molecules.

### Melt Compounding

A high molecular weight polymers such as polypropylene (PP), polyethylene (PE) and polystyrene (PS) and layered silicate mixture is annealed above the  $T_g$  or  $T_m$  of the polymer in either static or flow conditions. The filler is then kneaded and compounded thoroughly with the polymer melt in order to achieve a uniform dispersion and distribution of the filler.

### Sol-gel Technology

It consists of a direct crystallization of the silicate clays by hydrothermal treatment of a gel including polymer. Gels contain organics and organometallics, such as silica sol, magnesium hydroxide, lithium fluoride etc. It has the potential of promoting high dispersion of the silicate layers in one-step process, without requiring an anion as a surfactant. Of these melt compounding, twin-screw extruder is the most commonly used approach for generating polymer nanocomposites for the exfoliation and dispersion of silicate layers. Optimum residence time and shear intensity during processing are required to obtain the exfoliated and dispersed layered silicates. Melt processing is environmentally safe since no solvents are required, and gives freedom to end use manufacturers, and minimizes capital costs due to its compatibility with existing processes. Although the melt compounding approach requires high temperature for processing and it could thus result in surface modifications. Any degradation of the surface could have a serious impact on the composite properties and therefore one could use either a slightly lower temperature or more advanced thermally stable modifiers with optimal time scale.

### Nanocomposite Structures and Characterization

The microstructure of polymer nanocomposites owing to the interactions between organic polymer and inorganic filler phases is classified as intercalated, exfoliated, and unintercalated or microcomposites (Mittal V, 2008, Choi Y.S et al, 2004 & Gilman J.W et al, 2000) In the exfoliated structures, filler platelets are completely delaminated into their primary nanometer scale size and platelets are far apart from each other so that the periodicity of platelet arrangement is totally lost. This occurs when electrostatic forces of interaction between the platelets have completely been overcome by polymer chains. When a single or sometimes more than one extended polymer chain is intercalated into unaltered clay/ silicate layers interlayers, but the periodicity of the clay platelets is still intact, such a microstructure is termed as intercalated. The space occupied by polymer is typically in the order of a few nanometers. These systems display limited miscibility. This structure indicates that though the organic-inorganic hybrid is formed, electrostatic forces of interaction between the clay platelets could not however be totally dissolved. Based on the interfacial interactions and mode of mixing of organic and inorganic phases, it is possible that both the phases do not intermix at all and a microcomposite or unintercalated composite is formed. Figure 1 shows the schematic representation of the different types of composites generated based on the interactions of layered silicate with polymer matrices. (a) Phase separated microcomposite, (b) intercalated nanocomposite and (c) exfoliated nanocomposite. Nanocomposite could also be produced by dispersion of multi-layered silicate material into a thermoplastic polymer at a temperature greater than the melting or softening point of the thermoplastic polymer. Thermoplastic polymer is selected



Table 2. Comparisons of Thermoplastic and Thermosetting Resin Characteristics

Thermoplastic resin	Thermosetting plastic resin
High molecular weight solid	Low molecular weight liquid or solid
Stable material	Low to medium viscosity, requires cure
Re-processable, recyclable	Cross-linked, non-processable
Amorphous or crystalline	Liquid or solid
Linear or branched polymer	Low molecular weight oligomers
Liquid solvent resistance	Excellent environmental and solvent resistance
Short process cycle	Long process cycle
Neat up to 30% filler	Long or short fiber reinforced
Injection/compression/extrusion	Resin transfer molding (RTM)/filament winding (FW)/sheet molding compound (SMC)/pre-preg/ pultrusion
Limited structural components	Many structural components
Neat resin + nano-particles	Neat or fiber reinforced + nano-particles
Commodity: high-performance areas for automotive, appliance housings, toys	Commodity: advanced materials for construction, marine, aircraft, aerospace

from the group consisting of a thermoplastic urethane, a thermoplastic epoxy, polyester, nylon, polycarbonate and their blends.

Transmission electron microscopy (TEM) is commonly used method to characterize the microstructure of the nanocomposites. Owing to its accuracy and ease of operation, X-ray diffraction (XRD) is one of the most important techniques used for the characterization of the microstructure of the nanocomposites. The XRD quantifies the amount of increase in the basal plane spacing in the filler after surface modification as well as after the composite structure is formed. The increased basal plane spacing gives information regarding the

possible alignment of the modified molecules inside clay interlayers, whereas the presence or absence of diffraction peaks in the composites is used to assess information about microstructure of the composites.

#### Carbon nanotube-reinforced composites

Carbon nanotube has been the most promising materials in recently developed materials on account of its superior properties such as rigidity, strength, elasticity, electric conductivity and field emission. Carbon nanotubes (CNTs) are an allotrope of carbon (Figure 2). They take the form of cylindrical carbon molecules and have novel properties that make them potentially useful in a wide variety of applications such as nanotechnology, electronics, optics etc. Carbon Nanotubes have many structures, differing in length, thickness, and in the type of helicity and number of layers. Although they are formed from essentially same graphite sheet, their electrical characteristics differ depending on these variations, acting either as metals or as semiconductors. Nanotubes are

members of fullerene structural family, which also includes buckyballs. Whereas buckyballs are spherical in shape, a nanotube is cylindrical, with at least one end typically capped with a hemisphere of the buckyball structure (Iijima, S et al, 1993, Salvetat, J.P et al, 1999, Khan, U et al, 2007, Kearns, J.C & Shambaugh, R.L, 2002, Moniruzzaman M & Winey K.I, 2006, Khare Rupesh & Bose Suryasarathi , 2005).

Their name is derived from their size, since the diameter of a nanotube is on the order of a few nanometers (approximately 50,000 times smaller than the width of a human hair), while they can be up to several millimeters in length.

Carbon nanotubes are grown on silicon wafers by chemical vapor deposition (CVD) on which carbons are dissolved and precipitated in hexagonally packed graphite on the cooling surface side. Different ways for producing CNTs possess different genetic characters, such as single wall, multiple wall, conducting and semi-conducting. Carbon Nanotubes can be categorized by the following three structures:

- Single-wall Nanotubes (SWNT)
- Multi-wall Nanotubes (MWNT)
- Double-wall Nanotubes (DWNT)

Carbon nanotubes are highly conductive both to electricity and heat, with an electrical conductivity as high as copper and a thermal conductivity as great as diamond. They also have extraordinary mechanical properties and are 100 times stronger than steel with only

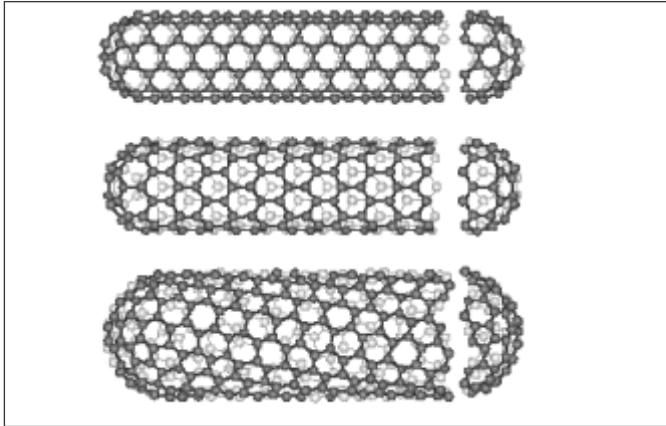


Figure 2. Single wall carbon nanotubes

one sixth of the weight and used for military, aerospace and medical applications in addition to its uses as lubricants, coatings, catalysts and electro-optical devices. Carbon Nanotubes show a unique combination of stiffness, strength, and tenacity compared to other fiber materials which usually lack one or more of these properties. Thermal and electrical conductivity are also very high and comparable to other conductive materials.

The use of carbon nanotubes as reinforcement filler-components is becoming more prominent for their mechanical characteristics especially in electronic applications like organic electronics and photovoltaics.

The CNT nano-fillers are dispersed within a polymer at a specified concentration and the entire mixture is fabricated into a composite. As grown CNT are processed into fibers or films, this macroscopic CNT material is then embedded into a polymer matrix. Published reports reveal that carbon nanotube-reinforced composites could be synthesized using a powder mixing process with a powder-powder blending between carbon nanotubes and ceramic powder or raw metal like aluminum or copper matrix followed by a conventional sintering process. However, characterization of these carbon nanotube-reinforced composite materials has shown a decrease in mechanical properties. In particular, relative density of the sintered composite materials becomes very low, ranging from 85% to 95%, which is important since low relative density means existence of many fracture sources, such as pores and defects, which could result in low mechanical properties. The reasons behind these problems are due to severe agglomeration of carbon nanotubes on the metal powder surface and the use of conventional consolidation processes.

The carbon nanotubes agglomeration in a metal matrix could be prevented by their homogeneous dispersion. For homogeneous dispersion, carbon nanotubes may be dispersed in a predetermined dispersing solvent like water, ethanol, nitric acid solution, toluene, N,N-dimethylformamide, dichlorocarbene and thionyl chloride to form a dispersed solution, which is further treated with ultrasonic wave. Water-soluble metal salts or metal hydrates are mixed with the ultrasonic wave treated dispersed solution, dried to remove water vapor, hydrogen, nitrogen and finally calcinated to produce a stable carbon nanotube / metal oxide nanocomposite powder.

Metal nanocomposite powders can be used as high-valued abrasive materials or wear-resistant coating materials. These could further be applied in areas, which use conventional metal composites, such as

the aerospace, high-performance machine parts, and medical industry, because it has high sintering performance.

### Polymeric Nanocomposites

Both thermoplastic and thermoset based nanocomposites have been widely studied, showing that in most cases the improvement of properties is counterbalanced by an increase in viscosity, modification of characteristic transition temperatures, loss of transparency and decrease of the polymerization kinetics. For this reason, research focuses has been on using alternative materials for the production of polymer nanocomposites by adding organic fillers or use of different types of inorganic nanofillers. Among the inorganic nanofillers, graphene has attracted great attention in recent years due to its exceptional thermal, mechanical, and electrical properties (Mark J.E et al, 1984, Nair CPR et al, 2001).

Several methods such as melt blending, solution mixing, coating, in-situ polymerization, nano-infusion etc. have been reported in the literature. The nanocomposites prepared using the above mentioned methods have huge potential for applications in automotive (seat frames, battery trays, bumper beams, load floors, front ends, valve covers, rocker panels and under engine covers, etc), aerospace (missile and aircraft stabilizer fins, wing ribs and panels, fuselage wall linings and overhead storage compartments, ducting, fasteners, engine housings and helicopter fairings etc.), optical devices, electrical and actuator devices and as flame retardant material.

Thermoplastic materials could be classified as metals, ceramics or polymers. However, the lower densities of polymeric materials offer an added advantage in applications where lighter weight is desired. The addition of thermally and/or electrically conducting fillers helps in developing conducting type nanocomposites. The property comparison between thermoplastic & thermoset resins is given in Table 2.

### Nylon 6 Nanocomposites

Mica-type silicates are attractive nano-clays functioning as reinforcing fillers for polymers because of their high aspect ratio and unique intercalation and exfoliation characteristics. The incorporation of organoclays into polymer matrices has been known for many decades. In 1976, Fujiwara and Sakomoto of Unitika patented first organoclay hybrid nanocomposite. Ten years later, a Toyota research team disclosed improved methods of producing nylon 6-clay nanocomposites using in-situ polymerization. The resulting nylon 6-clay nanocomposites exhibited increased solvent resistance, reduced permeability and increased flame retardance characteristics. Nanocomposites could also be obtained by direct polymer intercalation, where polymer chains diffuse into space between the clay galleries. This process could be combined with conventional polymer extrusion to reduce the time to form these hybrids, by shearing clay platelets leading to sample uniformity (Yang JL et al, 2006)

Dennis and Paul et al. demonstrated that both the chemistry of clay surface and type of extruder with its screw design affect the degree of exfoliation and dispersion of layered silicate nanocomposites formed from polyamide 6. Excessive shear intensity or back mixing also causes poor exfoliation and dispersion. The exfoliation and dispersion could be improved by increasing mean residence time in the extruder. Increased residence time in a low-shearing or mildly shearing environment allows polymer to enter the clay galleries and peel the platelets apart. It is reported that the non-intermeshing, twin-screw extruder yields the best exfoliation and

uniformity of dispersion.

### Clay-Based Nanocomposites

Clay minerals are the layered silicates comprising regular stacks of alumino-silicate layers. They have high aspect ratio and large surface area. The layers/platelets are built from octahedral and tetrahedral sheets. In the tetrahedral sheets silicon atom is surrounded by four oxygen atoms, whereas in the octahedral sheets, metal like aluminum or magnesium is surrounded by eight oxygen atoms. The difference in valences of Al and Mg creates negative charges distributed within the plane of the platelets that are balanced by positive counterions, typically sodium ions, located between the platelets (Arunkumar Lagashetty and A Venkataraman, July 2005).

Clay based nanocomposites have gained interest due to their exceptional properties like higher mechanical strength and thermal resistance of polymeric materials. These properties could further be improved by incorporating certain amount of clay in the polymeric materials. The variables such as type of clay, the choice of clay pre-treatment method, selection of polymer component and the way in which the polymer is incorporated has profound influence on the nature and properties of the final nanocomposite. The purity of the clay and homogeneity of dispersion of clay also affect the properties of nanocomposite. Polymer and clay are intrinsically non-miscible due to difference in their polarity. Polymers constitute non-polar, organic material whereas the clay is more polar and inorganic material. Therefore for successful formation of polymer-clay nanocomposites, clay polarity needs to be altered to make the clay 'organophilic'. This could be carried out by using swelling agents like surfactants which increases the interlayer distance of clay structure before it is mixed with a monomeric material, which is then polymerized in the presence of the clay to form nanocomposites.

The clay-based nanocomposite could be produced in the form of an intercalated or exfoliated hybrid structure. In the case of an intercalate, the organic component could be inserted between the layers of the clay such that the inter-layer spacing is expanded, but the layers still bear a well-defined spatial relationship to each other. In an exfoliated structure, the layers of the clay are completely separated and the individual layers are distributed throughout the organic matrix. Complete clay particles could also be dispersed within the polymer matrix as conventional filler.

Whether particular organo-clay hybrid nanocomposites are synthesized as an intercalated or exfoliated structure depends on the exchange capacity of the clay, polarity of the reaction medium and the chemical nature of the interlayer cations. Polymers can be introduced either by melt blending for example extrusion or by solution blending. Melt blending (compounding) depends on shear rate which help delaminate the clay and can be less effective than in situ polymerization in producing exfoliated clay based nanocomposite. The nature of the extruder and the screw configuration are important to achieve good organo-clay dispersion. Most of the studies have been performed on polymers/polymer blends like polystyrene (PS), polypropylene (PP), epoxy resins, polyamides, PVC,

PET, polysiloxanes, polyesters, nitrile rubbers, polyurethanes, PS-PMMA blends, polyamide 6-PP blends, polyisoprene-PEO blends. These novel materials have shown drastic enhancements in the mechanical, electrical, optical and thermal properties. For example, dramatic improvements in the stiffness and strength, increased dimensional stability, improved flame retardance, improved solvent and UV resistance, and reduction in permeability of gases have been reported. Even hyperbranched polymer/clay nanocomposites have been synthesized and exhibit enhancement in their properties.

### Thermoset based Nanocomposites

Thermoset nanocomposites are complex hybrid materials, which integrate nano-particles with polymers to produce a novel nano-structure, with extraordinary properties. Thermoset polymer nanocomposites have received less interest in their scientific development and engineering applications than their thermoplastic counterparts. However, some of these materials could be relatively easy to bring into production. The understanding of characteristics of the inter-phase region and the estimation of technology-structure-property relationships are the current frontier researches in thermoset nanocomposites (Muhammad Iftikhar Faraz, 2013)

The experimental results of work on thermoset nanocomposites and analyses obtained from the collaboration of three research groups from Bulgaria, Greece and Italy reported that the engineering resin nanocomposites are restricted to the most commonly used thermosets, such as epoxy resins, unsaturated polyesters, acrylic resins, and so on. Various nano-particles have been found to be useful for nanocomposite preparation with thermosetting polymers, along with smectite clay, diamond, graphite, alumina and ferroxides.

Thermoset nanocomposites results in improved dimensional/thermal stability, flame retardance and chemical resistance and have potential applications in marine, industrial and construction markets. The materials are eminently processable and can be shaped in conventional shaping steps, such as injection molding and extrusion processes. Shaped articles of a variety of natures can be manufactured from such nanocomposite materials e.g. fibers, packaging materials and construction materials.

### Areas of Applications

The commercial applications of nanocomposites have been growing at a rapid rate (Professor J.N Hay and S.J Shaw, 2001).

The worldwide production of nanocomposites has been estimated to exceed 600,000 MT and is set to cater to the following key areas in the near future:

- Drug delivery systems
- Anti-corrosion barrier coatings
- UV protection gels
- Lubricants and scratch free paints
- New fire retardant materials
- New scratch/abrasion resistant materials
- Superior strength fibres and films

Improvements in mechanical property have resulted in major interest in nanocomposite materials in numerous automotive and general/industrial



applications. These include potential for utilization as mirror housings on various vehicle types, door handles, engine covers and intake manifolds and timing belt covers. More general applications currently being considered include usage as impellers and blades for vacuum cleaners, power tool housings, mower hoods and covers for portable electronic equipment such as mobile phones, pagers etc.

### **Food Packaging**

The gaseous barrier property improvement that can result from incorporation of relatively small quantities of nanoclay materials has been shown to be substantial. Data provided from various sources indicate oxygen transmission rates for polyamide-organoclay composites, which are usually less than half of that in the unmodified polymer. Further data reveal the extent to which both the amount of clay incorporated in the polymer, and aspect ratio of the filler contribute to overall barrier performance. In particular, aspect ratio has been shown to have a major effect, with high ratios (and hence tendencies towards filler incorporation at the nano-level) quite dramatically enhancing gaseous barrier properties. Development of a combined active/passive oxygen barrier system for polyamide-6 materials is underway at various laboratories across the world. Passive barrier characteristics are provided by nanoclay particles incorporated via melt processing techniques whilst the active contribution comes from an oxygen-scavenging ingredient. Increased tortuosity provided by the nanoclay particles essentially slows oxygen transmission through the composite and drives molecules to active scavenging species resulting in near zero oxygen transmission for a considerable period of time.

Such excellent barrier characteristics have resulted in considerable interest in nanoclay composites in food packaging applications, both flexible and rigid. Specific examples include packaging for processed meats, cheese, confectionery, cereals and boil-in-the-bag foods, also extrusion-coating applications in association with paperboard for fruit juice and dairy products, together with co-extrusion processes for the manufacture of beer and carbonated drinks bottles. The use of nanocomposite packaging is expected to considerably enhance the shelf life of many types of food.

### **Fuel Tanks**

The ability of nanoclay incorporation to reduce solvent transmission through polymers such as polyamides has been demonstrated. Available data reveal significant reduction in fuel transmission through polyamide-6/66 polymers by incorporation of nanoclay filler. As a result, considerable interest is now being seen in these materials as both fuel tank and fuel line components for cars. The reduced fuel transmission characteristics are further accompanied by significant reduction in material cost.

### **Films**

In comparison to conventionally filled polymers, nanoclay incorporation has been shown to significantly enhance transparency and reduce haze. With polyamide based composites, this effect has been due to modifications in the crystallization behaviour brought out by the nanoclay particles. Similarly, nano-modified polymers when employed to coat polymeric transparency materials enhance both toughness and hardness of these materials without interfering with light transmission characteristics. Their ability to resist high

velocity impact combined with substantially improved abrasion resistance has also been demonstrated.

### **Environmental Protection**

Water laden atmosphere has long been regarded as a damaging environment for polymeric materials. Available data indicate that significant reduction of water absorption in a polymer could be achieved by nanoclay incorporation. Similar effects could also be achieved with polyamide-based nanocomposites. Specifically, increasing aspect ratio diminishes substantially the amount of water absorbed, thus indicating the beneficial effects likely from nanoparticle incorporation compared to microparticle loading. Nanocomposites exhibit excellent hydrophobicity thus reducing water transmission through an underlying substrate.

### **Flammability Reduction**

National Institute of Standards and Technology in the US has demonstrated that flammability behaviour could be restricted in polymers such as polypropylene with as little as 2% nanoclay loading. Heat release rates, as obtained from cone calorimetry experiments, were found to diminish substantially by nanoclay incorporation. Conventional microparticle incorporation, together with the use of flame retardant agents would also minimize flammability behaviour but this is usually accompanied by reductions in various important properties. With the nanoclay approach, fire retardance can be achieved whilst maintaining or enhancing other properties and characteristics.

## **Conclusions**

Nanotechnology has been revolutionizing the world of materials with its high impact in developing the new generation of composites with enhanced functionality and a wide range of applications. The investigations in processing, characterization and applications help researchers understand and utilize the special chemical and material principles underlying these polymer nanocomposites. Although nanocomposites are realizing many key applications in numerous industrial fields, an array of technical and economic barriers exists to their widespread commercialization. These include impact performance, complex formulation relationships and routes to achieving and measuring nanofiller dispersion and exfoliation in polymer matrix. Investment in state-of-the-art equipment and the enlargement of core research teams are other bottlenecks to bring out innovative technologies on nanocomposites. Future trends include extension of this nanotechnology to additional types of polymer system, where the development of new compatibility strategies would likely to be a prerequisite. Production of PVC-based systems is still some way off and challenges remain to be solved in PET nanocomposites. Additional reinforcement of clay nanocomposites by glass fibre is currently being investigated. There is also interest in the development of electrically conducting clay nanocomposites.

While considerable basic research activities are currently underway at Indian academic institutions & national research labs, immediate exercises on product development-cum-demonstration should be taken up in active collaboration with the industries in the country.

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