

Polymer nanocomposites preparation, characterization and application: An Overview

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ABSTRACT

Polymer nanocomposites (PNCs), defined as polymers bonded with nanoparticles to produce materials with enhanced properties, have been in existence for years but are recently gaining momentum in mainstream biosensor, drug delivery, gas barrier, commercial packaging, automobile, fuel and flame retardant materials industries. This article is designed to handover an extensive report on polymer nanocomposite research. It starts with a brief introduction of nanotechnology and nanocomposite to create a base for the better understanding of core of the subject. It discusses and correlates the scientific principles and mechanisms with various techniques for the synthesis of different PNCs. In this article, efforts are made to give necessary foundation and tools to address system-specific complexity and explain the properties of PNCs with the help of scientific framework which gives clues for the processing of PNC of desired and altered properties. Characterization techniques of these materials are briefly depicted and finally a summary of the vast commercial applications along with its health and safety concerns is. Thus this article offers the general discussion on polymer nanocomposites processing and synthesis, characterization and applications.

Key words: Nanocomposite; nanoparticle; metal-polymer; clay-polymer; CNT-polymer.

INTRODUCTION

Materials and their development are fundamental to society. Major historical periods of society are ascribed to materials (i.e., stone age, bronze age, iron age, steel age [industrial revolution]; silicon age and silica age [telecom revolution]). Scientists will open the next societal frontiers not by understanding a particular material, but rather by understanding and optimizing the relative contributions afforded by material combinations keeping a pace with current technology..

Nanotechnology

Nanotechnology is a field of applied science and technology covering a broad range of topics. The main unifying theme of this technology is the control of matter on a scale below 100 nanometers, as well as the fabrication of devices on this same length scale[1-3]. Despite the apparent

simplicity of this definition, nanotechnology actually encompasses a very diverse group of lines of inquiry, each taking different approaches and using different methods to progress towards different applications [4,5]. It is a highly multidisciplinary field, drawing from fields such as colloidal science, device physics, supramolecular chemistry to environment science demanding newer materials which can satisfy, follow and respond to the system conditions and principles at the nanoscale. It could variously be seen as an extension of existing sciences into the nanoscale, or as a recasting of existing sciences using a newer, more modern term. Visionaries such as Richard Feynman speculated about the future of unimaginably small devices as early as 1959. In a now famous talk entitled "There's Plenty of Room at the Bottom," Feynman urged his colleagues to invent new techniques that could control, manipulate, and fabricate devices with dimensions that were, at the time, unimaginable.

Nanocomposite

Materials with features on the scale of nanometers often have properties dramatically different from their bulk-scale counterparts. For example, nanocrystalline copper is five times harder than ordinary copper with its micrometer-sized crystalline structure. The development of such materials is currently a research area of great interest. Important among these nanoscale materials are *nanocomposites*, in which the constituents are mixed on a nanometer-length scale. In other words, Nanocomposites are materials that are created by introducing nanoparticulates into a macroscopic sample material (Fig.1). They often

have properties that are superior to conventional microscale composites and can be synthesized using surprisingly simple and inexpensive techniques. A nanoscale dispersion of sheet-like inorganic silicate particles in a polymer matrix, for example, is superior to either constituent in properties such as improved biodegradability, optical clarity, strength, stiffness, thermal stability, reduced permeability, and flame retardancy. Nature also makes fabulous nanocomposites, and scientists are trying to emulate such processes. The abalone shell, for example, has alternating layers of calcium carbonate and a rubbery biopolymer; it is twice as hard as and a thousand times tougher than its

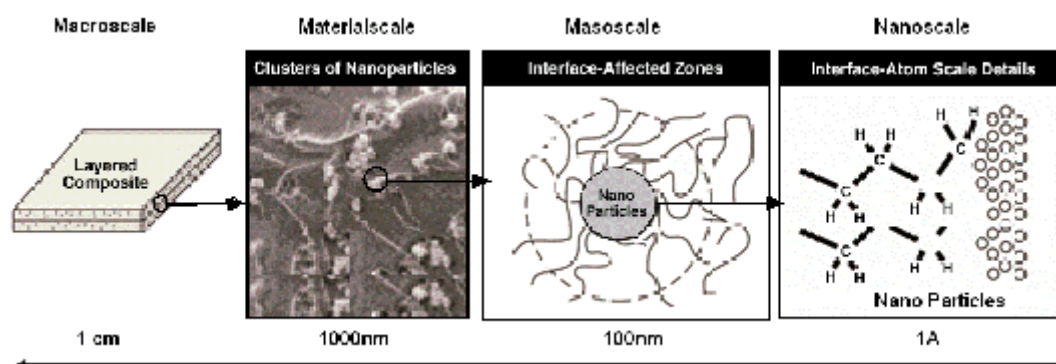


Fig. -1: Nano composite as a multilayer system.
From Macroscale composite structure to clustering of Nanoparticles

components. The definition of nano-composite material has broadened significantly to encompass a large variety of systems such as one-dimensional, two-dimensional, three-dimensional and amorphous materials, made of distinctly dissimilar components and mixed at the nanometer scale. Thus the study of nanocomposite materials requires a multidisciplinary approach, involving novel chemical techniques and an understanding of physics and surface science. 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. Experimental work has generally shown that virtually all types and classes of nanocomposite materials lead to new and improved

properties when compared to their macrocomposite counterparts.

Therefore, nanocomposites promise new applications in many fields such as mechanically reinforced lightweight components, biomedical systems, non-linear optics ⁶, battery cathodes and ionics, nano-wires, and sensors etc. Polymer-based nanocomposites are also being developed for electronics applications such as thin-film capacitors in integrated circuits and solid polymer electrolytes for batteries. There is also the possibility of new properties which are unknown in the parent constituent materials ^{7, 8}.

Polymer nanocomposite

Polymer Nanocomposites are comparatively a new class of composites, which are

particle-filled polymers for which at least one dimension of the dispersed particles is in the nanometer range⁹. One can distinguish three types of nanocomposites, depending on how many dimensions of the dispersed particles are in the nanometer range. When the three dimensions are in the order of nanometers, we are dealing with isodimensional nanoparticles, such as spherical silica nanoparticles obtained by in situ sol-gel methods^{9,10} or by polymerization promoted directly from their surface¹¹, but also can include semiconductor nanoclusters¹² and others¹⁰. When two dimensions are in the nanometer scale and the third is larger, forming an elongated structure, we speak about nanotubes or whiskers as, for example, carbon nanotubes¹³ or cellulose whiskers^{14,15} which are extensively studied as reinforcing nanofillers yielding materials with exceptional properties. The third type of nanocomposites is characterized by only one dimension in the nanometer range. In this case the filler is present in the form of sheets of one to a few nanometer thick to hundreds to thousands nanometers long. The reinforcement of polymers using fillers, whether inorganic or organic, is common in the production of modern plastics. Polymeric nanocomposites (PNCs) (or polymer nanostructured materials) represent a radical alternative to conventional-filled polymers or polymer blends. In contrast to the conventional systems where the reinforcement is on the order of microns, discrete constituents on the order of a few nanometers (~10,000 times finer than a human hair) exemplify PNCs¹⁶.

The key to the synthesis of nanocomposites is how the nanoparticulates are made to disperse in the sample material. For example, while studying the drug release behavior of clay-based poly(*N*-isopropylacrylamide) nanocomposite hydrogels for a few model drugs (i.e., neutral caffeine, cationic crystal violet and phenol red), they found that the drug release largely depended on the factors such as the content of clay and its intercalated agents, the charge of drug solute, interaction between the gel and drug solute, and ionic strength of the medium²².

Biomedical poly (urethane urea)s (PUU) are used in a variety of biomedical applications such as blood sacs in ventricular assist devices and total

artificial hearts. However, such elastomers have relatively high permeability to air and water vapor. One traditional approach to reducing permeability is to modify the chemistry of polymer. Recently, Manias and co-workers¹⁸⁻²⁰ reported a more efficient approach in which clay platelets were dispersed into polymer. The resulting polymer nanocomposites have showed significantly reduced (ca. five fold) gas permeability as well as the improvement in mechanical properties (e.g., stiffness, modulus). Such enhancements are beyond what can be achieved by chemical modification of polyurethanes. However, their biocompatibility for such polymer nanocomposites and high cycle fatigue resistance need to be confirmed. Polymer nanocomposites have recently been investigated for controlled drug delivery. Giannelis and co-workers²¹ reported that the addition of organoclays not only reduced the rate of drug (i.e., dexamethasone) release from the biocompatible poly(ethylene-co-vinyl acetate) matrix but also increased the Young's modulus as compared to the pure polymer. Lee and co-worker [22,23] fabricated a series of clay-based poly (*N*-isopropylacrylamide) nanocomposite hydrogels and investigated their swelling and drug release behaviors. It was shown that the increase in the content of either intercalated quaternary ammoniums in organoclays or clay in nanocomposites led to the decrease in swelling ratio of the nanocomposite hydrogels but the increase in the gel strength.

Considering the plurality of potential nanoparticles, polymeric resins, and applications, the field of PNCs is immense. For example, Fig. 2 presents a hierarchy of nanoparticles based on increasing functionality and thus, the potential to increase the functionality of the polymer matrix. Several types of polymeric nanocomposite can be obtained with different particle size, nature and shape;

- Clay-Polymer Nanocomposites;
- Metal-Polymer Nanocomposites;
- Carbon Nanotubes-Polymer Nanocomposites

Clay-Polymer Nanocomposites

Clay minerals, due to their unique layered structure, rich intercalation chemistry and availability at low cost, are promising nanoparticle reinforcements for polymers to manufacture low-

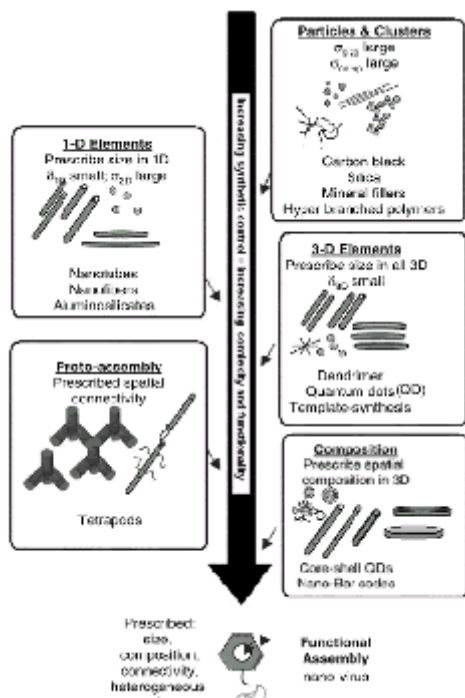


Fig. - 2: Categorization of nanoparticles based on increasing functionality and thus, potential to increase functionality of the polymer matrix, which in turn is based on increasing spatial and compositional precision in nanoparticle fabrication. Increased complexity and function require increased synthetic control. Nanoscale particles and clusters are polydisperse in size (σ_{size}) and composition (σ_{comp}). One-dimensional elements are compositionally uniform, with narrow size dispersion in one dimension ($\delta 1D$), but polydisperse in the other two ($\delta 2D$). Threedimensional elements exhibit narrow size dispersion in all dimensions ($\delta 3D$). Rather than compositional uniformity, prescribed composition variation in three dimensions results in tailored functionality, where proto-assembly of any of the aforementioned elements enables the creation of an infinite variety of tailored nanoparticles. Finally, the ultimate active and functional nano-unit would embody the characteristics of a virus – prescribed size, composition, site-specific surface functionality, and dynamic responsiveness leading to alteration of the particle's properties, composition, or size.

cost, lightweight and high performance nanocomposites. Clay minerals used for polymer nanocomposites can be classified into three groups. They are (1) Type I, (2) Type II and (3) Layered silicic acids. Their structures (Fig.3) are briefly

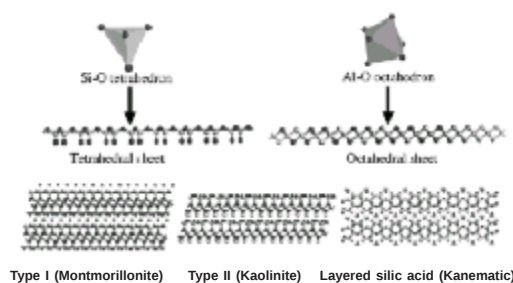


Fig. -3: Structure of clay minerals represented by montmorillonite, kaolinite and kanemite. They are built up from combinations of tetrahedral and octahedral sheets whose basic units are usually Si-O tetrahedron and Al-O octahedron, respectively.

described as follows. Type I: The clays belong to the smectite family with the crystal structure consisting of nanometer thick layers (platelets) of aluminium octahedron sheet sandwiched in between two silicon tetrahedron sheets. Stacking of the layers leads to a van der Waals gap between the layers. Isomorphic substitution of Al with Mg, Fe, Li in the octahedron sheets and/or Si with Al in tetrahedron sheets gives each three-sheet layer an overall negative charge, which is counterbalanced by exchangeable metal cations residing in the interlayer space, such as Na, Ca, Mg, Fe, and Li. Type II: The clays consist of layers made up of one aluminium octahedron sheet and one silicon tetrahedron sheet. Each layer bears no charge due to the absence of isomorphic substitution in either octahedron or tetrahedron sheet. Thus, except for water molecules neither cations nor anions occupy the space between the layers, and the layers are held together by hydrogen bonding between hydroxyl groups in the octahedral sheets and oxygen in the tetrahedral sheets of the adjacent layers. Layered Silicic Acids: The clays consist mainly of silicon tetrahedron sheets with different layer thickness. Their basic structures are composed of layered silicate networks and interlayer hydrated alkali metal cations. The silanol groups in the

interlayer regions favor the organic modification by grafting organic functional groups in the interlayer regions. They are natural clay minerals except for octosilicate, but can be synthesized as well. Layered silicic acids are potential candidates for the preparation of polymer nanocomposites because they exhibit similar intercalation chemistry as smectite clays. They possess high purity and structural properties that are complementary to smectite clays. Typically smectite-type clays are used as fillers and such montmorillonite and hectorite layered structure are dispersed in polymer matrix. Accordance with the bonding scenarios between polymer chain and silicate layer, new material shows excellent mechanical characteristics (e.g. 40% increase in room temperature tensile strength), heat resistance (e.g. 100% increase in the heat distortion temperature) and chemical resistance (e.g. ~10 fold decrease in O_2 and H_2O permeability) compared to the neat or traditionally filled resins. These property improvements result from only a 0.1-10 vol. % addition of the dispersed nanophase. Polyimide-clay hybrids represent another example of polymer nanocomposites. The claypolyimide hybrid composite films exhibit greatly improved CO_2 barrier properties at low clay content; less than 8.0 vol. % clay results in almost a ten-fold decrease in permeability. Another interesting and exciting property is the significantly improved biodegradability of nanocomposites made from organoclay and biodegradable polymers. Tetto *et al.*,²⁴ first reported studies on the biodegradability of nanocomposites based on PCL, which showed an improved biodegradability over pure PCL. Such an improved biodegradability of PCL in clay-based nanocomposites may be attributed to a catalytic role of the organoclay in the biodegradation mechanism. It is clear that polymer/clay nanocomposites are a typical example of nanotechnology; embedding nanoclay structure in polymer matrix, a new class of materials is obtained.

Fabrication techniques of polymer-clay nanocomposite

In order to disperse clay layers into polymer matrix it's very important considering polymer-clay compatibility. This means to provide organophilic character to the clay by a pretreatment in order to successful formation of polymer-clay nanocomposite. Most polymers are hydrophobic

and are not compatible with hydrophilic clays. Pretreatment is a process in which organophilic clay is formed from hydrophilic clay using amino acids, organic ammonium salts, or tetra organic phosphonium solution. While in the case of hydrophilic polymers and silicate layers, pretreatment is not necessarily required.

Several strategies have been considered to prepare polymer-layered silicate nanocomposites^{25,26,37}. They include four main processes²⁷.

Exfoliation-adsorption

The layered silicate is exfoliated into single layers using a solvent in which the polymer (or a prepolymer in case of insoluble polymers such as polyimide) is soluble. It is well known that such layered silicates, owing to the weak forces that stack the layers together can be easily dispersed in an adequate solvent. The polymer then adsorbs onto the delaminated sheets and when the solvent is evaporated (or the mixture precipitated), the sheets reassemble, sandwiching the polymer to form, in the best case, an ordered multilayer structure. Under this process are also gathered the nanocomposites obtained through emulsion polymerization where the layered silicate is dispersed in the aqueous phase [Fig. 4]. This technique has been widely used with water-soluble polymers to produce intercalated nanocomposites^{28,29} based on poly(vinyl alcohol) (PVOH)^{30,31}, poly(ethylene oxide) (PEO)^{31,32}, poly(vinylpyrrolidone) (PVPyr)³³ or poly(acrylic acid) (PAA)³².

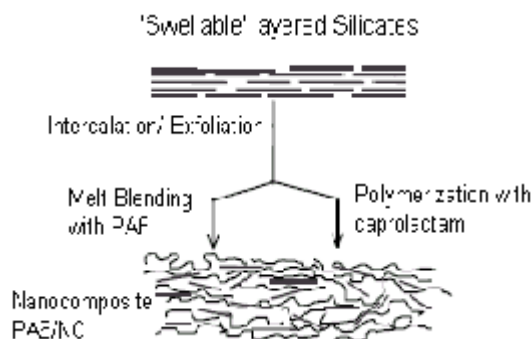


Fig. - 4: Formation of Nanocomposite from swellable layered silicates

In situ intercalative polymerization

In this technique, the layered silicate is swollen within the liquid monomer (or a monomer solution) so as the polymer formation can occur in between the intercalated sheets. Polymerization can be initiated either by heat or radiation, by the diffusion of a suitable initiator or by an organic initiator or catalyst fixed through cationic exchange inside the interlayer before the swelling step by the monomer. Many interlamellar polymerization reactions were studied in the 1960s and the 1970s using layered silicates (see ref. ³⁴ and references therein) but it is with the work initiated by the Toyota research team ^{35,36} that the study of polymer-layered silicate nanocomposites came into vogue about 10 years ago. They studied the ability of Na-montmorillonite organically modified by protonated α,ω -aminoacid ($H_3N-(CH_2)_{n=1-10}-COOH$, with $n=2, 3, 4, 5, 6, 8, 11, 12, 18$) to be swollen by the ϵ -caprolactam monomer (melting temperature, 708°C) at 100°C and subsequently to initiate its ring opening polymerization to obtain nylon-6-based nanocomposites^{36,38}. Recently, with this method Messersmith and Znidarsich ³⁹ investigated the feasibility of developing polymer nanocomposites capable of altering their structure and properties upon the application of external stimulus.

Melt intercalation

The layered silicate is mixed with the polymer matrix in the molten state. Under these conditions and 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. In this technique, no solvent is required. Vaia and Giannelis⁴⁰ have studied polystyrene (PS) as the matrix for dispersing different types of clays. Lifluorohectorite (CEC.150 meq/100 g), saponite (100 meq/100 g), and sodium montmorillonite (80 meq/100 g) were accordingly modified using various ammonium cations: dioctadecyldimethylammonium, octadecyltrimethylammonium, and a series of primary alkylammonium cations with carbon chains of 6, 9-16 and 18 carbon atoms. The co-intercalation of poly(methyl methacrylate)⁴¹ claimed to be a potential way to enhance the ionic conductivity of polymer-layered silicate nanocomposites.

Template synthesis

This is a technique, where the silicates are formed in situ in an aqueous solution containing the polymer and the silicate building blocks has been widely used for the synthesis of double-layer hydroxide-based nanocomposites^{42,43} but is far less developed for layered silicates. In this technique, based on self-assembly forces, the polymer aids the nucleation and growth of the inorganic host crystals and gets trapped within the layers as they grow. This method is particularly adapted to water soluble polymers, and some attempts have been achieved with polymers such as poly(vinylpyrrolidone) (PVPyr), hydroxypropylmethylcellulose (HPMC), poly(acrylonitrile) (PAN), poly(dimethyldiallylammonium) (PDDA) and poly(aniline) (PANI)⁴⁴.

Several other methods like sonication, adsorption via sonication, extrusion and spin casting techniques have been also reported as better methods to prepare polymer/clay nanocomposites.

In reality, mechanical properties in the best clay-polymer nanocomposites are much lower than conventional fiber reinforced composites. Only in the low filler range 4% nanocomposites show better mechanical performance. To obtain higher performance it requires to add more filler, but adding more fillers ascend more complicated physical-technological problem occur. The surface area of the silicate-filler increases with the increasing reinforcing load, leading to insufficient polymer molecules to wet enormous clay surface.

Data provided by Hartmut Fischer of TNO in the Netherlands relating to polyamide – montmorillonite nanocomposites indicates tensile strength improvements of approximately 40 and 20% at temperatures of 23°C and 120°C respectively and modulus improvements of 70% and a very impressive 220% at the same temperatures. In addition Heat Distortion Temperature was shown to increase from 65°C for the unmodified polyamide to 152°C for the nanoclay-modified material, all the above being achieved with just a 5% loading of montmorillonite clay (Fig.5). Similar mechanical property improvements were presented for polymethyl methacrylate - clay hybrids.

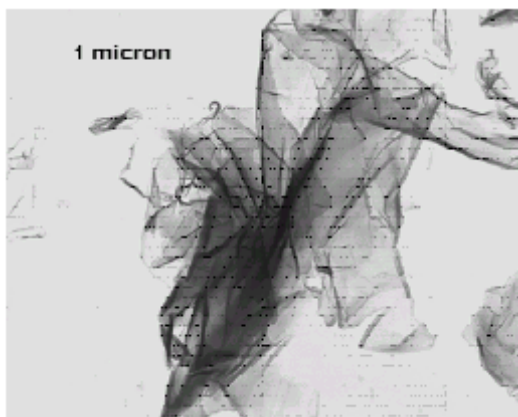


Fig. -5: TEM micrograph of the morphology of montmorillonite clay

Further data provided by Akkepeddi of Honeywell relating to polyamide-6 polymers confirms these property trends. In addition, the further benefits of short/long glass fiber incorporation, together with nanoclay incorporation, are clearly revealed.

Few difficulties especially the fabrication problem are being faced in dealing with thermosetting polymers and the thermally instability of organoclay. But the major difficulties of the development of clay/polymer nanocomposites are caused due to the poor understanding the primary mechanisms of nano-world.

Metal/particle-Polymer Nanocomposites

Metal-Polymer Nanocomposites are the materials in which the constituent polymers contain transition metal complexes either attached to or directly in a π -conjugated backbone². The usual term "material"; refers to an almost infinite number of constituents (e.g. atoms, molecules) displaying an averaged statistical behavior. The embedded metal nanoparticles, profoundly affect polymers' typical mechanical and physical properties (glass transition, crystallinity etc.) The macromolecules in Metal/ Polymer Nanocomposites are hybrid of π -conjugated organic and transition metal containing polymers, π -conjugated organic polymers, such as polyacetylene, polythiophene, and polypyrrole, as well as oligomers and derivatives of these materials have been extensively explored. These materials

are endowed with many important properties such as nonlinear optical properties⁴⁵, electronic conductivity⁴⁶ and luminescence, and have been proposed for their use in various applications including biochemical sensors, electroluminescent devices biomolecular sensors, electro catalysis, batteries, smart windows and memory devices. Fluorescence spectroscopy with molecular probes is an attractive method for monitoring biochemicals due to high sensitivity and specificity. For this, fiber optic probes with charged molecules are attractive for chemical and biosensing applications. Fluorescent sensors based on polymer/polymer-dye multilayers, and plasmonic sensors based on polymer/nanoparticles-antibody nanocomposites have been produced using Layer-by-Layer self-assembly (LBL) method for depositing ultra thin film on the tips of optical fibers. Multilayer fluorescent nanocomposite films containing bis(Z,2'-bipyridine) 4'-methyl-4-carboxybipyridineruthenium-N-succinimidyl-ester bis(hexafluoro-phosphate) (Ru(bpy)Z(mcbpy)) conjugated to poly(allylamine hydrochloride) (PAH) and Alexa 4WM conjugated to PAH were combined for an oxygen sensor. In a separate demonstration, gold nanoparticle multilayers were combined with an anti-IgG outer coating to realize a novel surface plasmon resonance (SPR)-based detector.⁴⁷ bio6 dye]. Biosensors utilizing various electrostatically complexed redox polymer and enzyme couples have been successfully used to detect glucose, lactate and other analytes. Pishko et al⁴⁸ described mass transfer and hydrogel swelling in electrostatically assembled nanocomposite thin films consisting of alternating layers of an organometallic redox polymers, poly[vinylpyridine Os(bis-bipyridine)2Cl-co-allylamine] (PVP-Os-AA) and oxidoreductases enzymes GOX, LAX and PYX. The scheme used for fabrication of these sensors is based upon electrostatic attraction between a polycationic osmium redox polymer and a polyanionic enzyme, GOX, LAX or PYX. A schematic of a final nanocomposite structure is shown in Figure 6. Combined electrochemistry and SPR was used to observe structural changes in the nanocomposite films resulting from the movement of water and ions into and out of the film and confirmed that the film structure imposes mass transfer limitations, suggesting that it is highly compact and may be nanoporous⁴⁹.

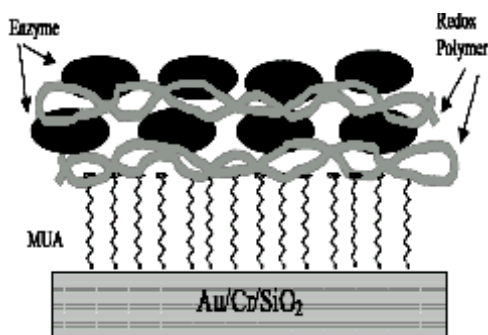


Fig. -6: Schematic of the nanocomposite structure created by the layer-by-layer deposition of alternating polyanionic MUA (11-mercaptoundecanoic acid) and polycationic films on gold.

Physical and chemical properties of metal nanoparticles

The specific-size dependence of these properties becomes evident when they:

- no longer follow classical physical laws but rather are described by quantum mechanical ones; are dominated by particular interface effects;
- exhibit properties due to a limited number of constituents

Fabrication Techniques of Metal Polymer Nanocomposite

The nanoparticles size and shape are very important in order to obtain predefined properties of nanomaterials. At present, two different techniques are being extensively used to obtain metal-polymer nanocomposites:

- *In-Situ* synthesis method.
- *Ex-Situ* synthesis method

In the *in-situ* technique

Nanoparticles are generated inside polymer matrix by decomposition of metal precursors. In the *in situ* methods, two steps are needed: First, monomer is polymerized in solution containing metal ions chemical species, then metal nanoparticles are obtained by reducing metal ions through chemical⁵⁰⁻⁵², thermal⁵³ or photolysis or by UV Irradiation⁵⁴ methods⁵⁵. In situ polymerization is limited by two factors: (i) the distance from monomer to monomer when it is strongly anchored (or grafted)

to the host matrix, i.e., its degree of freedom; (ii) the condition that the polymerization (temperature, pH, or redox reaction) must leave the layered structure intact⁵⁶.

Polyacrylamide(PAM)–semiconductor MS (M = Cd, Zn, Pb) nanocomposites with homogeneously well dispersed semiconductor nanoparticles in the polymer matrices were prepared by a novel *in situ* simultaneous polymerization– hydrolysis technique (SPH)⁵⁷. This SPH technique provides a new route to prepare other metal sulfide–polymer hybrid nanocomposites⁵⁸.

In the ex-situ technique

Nanoparticles are produced by chemical methods first and then are distributed into a polymer solution or monomer solution to polymerize. Usually, the ex-situ techniques for the synthesis of metal/polymer nanocomposites are preferred to the *in situ* methods because of the high optical quality that is achieved in the final product prepared by ex-situ techniques^{59,60}.

Other techniques have also been studied in order to obtain optimal properties controlling size and shape of nanoparticles in matrix or polymeric film (e.g Vapor deposition, cryochemical synthesis). The morphology of Ag nanoparticles in Ag/polyaniline nanocomposites prepared by γ -ray irradiation⁶¹ is studied recently.

Carbon Nanotubes-Polymer Nanocomposites

Carbon nanotubes (CNTs) exhibit unique mechanical, electronic and magnetic properties, which have caused them to be widely studied ⁶². CNTs are probably the strongest substances that will ever exist with a tensile strength greater than steel, but only one sixth the weight of steel⁶³. Iijima (1991) first discovered carbon nanotubes (CNTs) using arc discharge method. Since carbon–carbon covalent bonds are one of the strongest in nature, a structure based on a perfect arrangement of these bonds oriented along the axis of nanotubes would produce an exceedingly strong material. These nanotubes are strong and resilient structures that can be bent and stretched into shapes without catastrophic structural failure in the nanotubes^{64, 65}. The Young's modulus and tensile strength rival that

of diamond (1 Tera Pascal and ~200 Giga Pascal, respectively)⁶⁶. In the technological field of polymer nanocomposites, new potential applications may be obtained using carbon nanotubes as reinforced nanofibers and to impart unique properties to the polymer matrix. The extent of property enhancement of such a nanotube polymer nanocomposite depends on a number of factors; the most important are the extent of nanotube dispersion in the polymer matrix and the interaction between the nanotubes and the host polymer. A homogeneous, uniform dispersion of the nanotubes in the polymer matrix, with significant interactions between them, is desirable in creating an optimal nanocomposite as shown in Fig. 7.

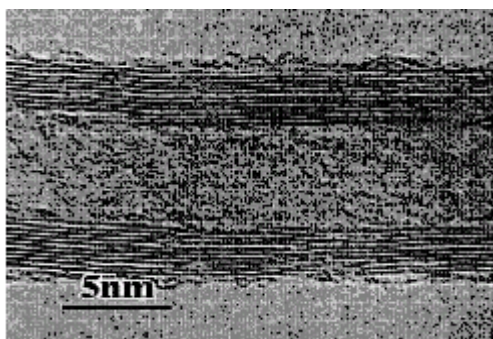


Fig. - 7: TEM micrograph showing the layered structure of a multiwalled carbon nanotube.

The nanotubes exfoliation into a polymer matrix and its effect on mechanical properties has been reported⁶⁷. Due its typical structure with high aspect ratio and anisotropic structure, carbon nanotubes show characteristic electrical and thermal properties also. After verification of extraordinary mechanical properties of carbon nanotubes and its electrical conductivity and thermal properties, great excitement is arisen among researcher considering potential applications of CNT/Polymer nanocomposite⁶⁸⁻⁷¹.

Wegner *et al*⁷² have dispersed single-wall carbon nanotubes in amorphous polymers to study their properties by specifically developed fabrication methods in which the resulting nanocomposites were melt-spun into fibers or hot-pressed to films and then into sheets. Recently, for making chemical capacitor, testing of a PANI/SWNTs composite obtained by the chemical polymerization of aniline

in the presence of SWNTs has been carried out⁷⁸. The composite electrode shows high specific capacitance, better power characteristics and is more promising for application in capacitor than pure PANI electrode. Other supercapacitor electrodes were fabricated using a solution of high molecular weight PANI which was added at various weight percentages of SWNTs⁷³. Current-voltage (I-V) characteristics of these devices indicate a significant growth in current as the CNs concentration increases in the composite. A new supercapacitor electrode based on a PEDOT/MWNTs nanocomposite was reported in 2004 by Lota *et al.*⁷⁴. Many amperometric biosensors, particularly the oxidase-based ones, require the use of charge-transfer mediators or electrocatalysts. To be efficient, these latter should be immobilized in the close vicinity of the electrode surface while keeping mobile enough to facilitate communication between the active sites of the biomolecule and the electrode surface. The use of MWNTs provides a novel electrode platform for polymer-based biosensors⁷⁵. An example in this sense is the PPY based glucose oxidase system for detection of glucose. Xi-Liang *et al* proposed simple and controllable electrodeposition method for the formation of a chitosan-carbon nanotube nanocomposite film on an electrode surface was proposed and further used for the construction of an electrochemical biosensor⁷⁶. Tsai *et al* has prepared nanocomposite film of multi-walled carbon nanotubes (MWNTs) with NafionTM by cast deposition on glassy carbon electrodes (GCE). Their study indicates that the electroanalytical nanocomposite film composed of MWNTs and NafionTM is highly sensitive and suitable for potential electrochemical sensor applications⁷⁷. In general, CNTs are considered good transducers, stabilizer and mediators for biosensor applications.

Even though carbon nanotubes have already been blended within various polymers, homogeneous dispersion of the nanotubes in the polymer matrix remains one major challenge, since bundles of aggregated SWNTs or MWNTs most often persist and therefore limit the performances of the recovered composite materials.

So far, in contrast of layered silicate polymer nanocomposites, applications of carbon nanotubes have been hindered mainly due to

production and synthesis problems. In fact Carbon Nanotubes became available commercially only in recent days and with limited quantity. The successful production of Carbon Nanotubes with specific dimensions and physical properties is not achieved yet. For this reasons in the last decades many research program has been developed in order to produce and to effective use of carbon nanotubes capacity. Potential applications go beyond mechanical reinforced nanomaterials from antistatic film packaging to every application in well established electrical, optical and thermal properties of carbon nanotubes.

Polymers nanocomposite and classic filled systems

Whether tubes (e.g. single- and multi-walled carbon nanotubes, SWNT and MWNTs, respectively) or plates (e.g. exfoliated graphite, layered silicates), the nanoscopic dimensions and extreme aspect ratios inherent in these nanofillers result in six interrelated characteristics distinguishing the resultant PNCs from classic filled systems:

- Low percolation threshold ($\sim 0.1-2$ vol%);
- Particle-particle correlation (orientation and position) arising at low volume fractions ($\phi_C < 0.001$);
- Large number density of particles per particle volume ($106-108$ particles/ μm^3);

- Extensive interfacial area per volume of particles ($103-104$ m^2/ml);
- Short distances between particles ($10-50$ nm at $\phi \sim 1-8$ vol%); and
- Comparable size scales among the rigid nanoparticle inclusion, distance between particles, and the relaxation volume of polymer chains.

For spherical nanoparticles, the first two characteristics are not commonly observed because of the small aspect ratio of the particle. Nevertheless, PNCs containing low-aspect ratio nanoparticles are a critical bridge between conventional micron-scale fillers and high-aspect ratio Nanoparticles where, from the nanoparticle perspective, size is reduced and number density is increased prior to the additional complexity of orientational correlations introduced by an extreme aspect ratio. The first two characteristics can manifest in spherical nanoparticles systems also, by innovative processing or proto-assembly of these nanoparticles. Overall, the key concept to answer 'what is a PNC' is not specifically embodied within the shape of the particle, but how do the characteristics of the particle provide a means to 'engineer and tailor morphology to achieve a desired property suite from the PNCs. To convey the origin and interrelation of these distinguishing

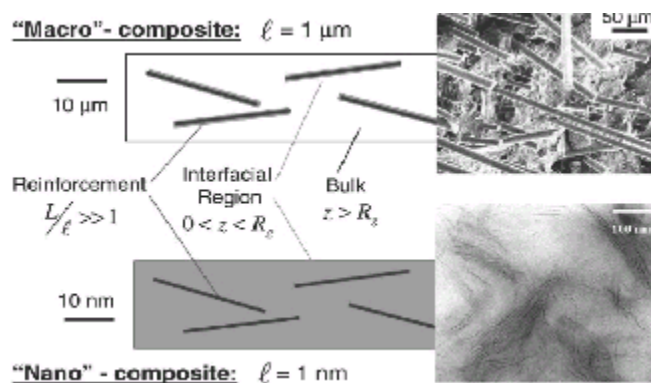


Fig. -8: Schematic comparison of a 'macro'-composite containing $1 \mu\text{m} \times 25 \mu\text{m} \times L$ fibers in an amorphous matrix to that of a 'nano'-composite at the same volume fraction of filler, but containing $1 \text{ nm} \times 25 \text{ nm}$ fibers. There are three main material constituents in any composite: the matrix (white), the reinforcement (fiber), and the so-called interfacial region, which extends (z) into the matrix on the order of R_g , the radius of gyration of the polymer. Scanning electron micrograph shows E-glass reinforced polyolefin ($15 \mu\text{m}$ fiber) and transmission electron micrograph shows montmorillonite-epoxy nanocomposite (1 nm thick layers)¹⁰⁴.

characteristics, Fig. 8 compares the dominant morphological scale of a classic filled polymer containing $1\ \mu\text{m} \times 25\ \mu\text{m}$ fibers in an amorphous matrix to that of a nano-filled system at the same volume fraction of filler, but containing $1\ \text{nm} \times 25\ \text{nm}$ fibers. There are three main material constituents in any composite: the matrix, the reinforcement (fiber), and the so-called interfacial region. The interfacial region is responsible for 'communication' between the matrix and filler and is conventionally ascribed properties different from the bulk matrix because of its proximity to the surface of the filler. Nominally, the spatial extent of this perturbed matrix is thought to extend into the bulk one to four times the radius of gyration of the matrix, R_g , which has a value of around tens of nanometers. For polymers, R_g is the key spatial parameter to which the majority of the polymer's static and dynamic properties can be ultimately related.

Nanocomposite structures

Depending on the nature of the components used (layered silicate, organic cation and polymer matrix) and the method of preparation, three main types of composites may be obtained when a layered clay is associated with a polymer (Fig. 9). When the polymer is unable to intercalate between the silicate sheets, a phase separated composite (Fig. 9a) is obtained, whose properties

stay in the same range as traditional microcomposites. Beyond this classical family of composites, two types of nanocomposites can be recovered. Intercalated structure (Fig. 9b) in which a single (and sometimes more than one) extended polymer chain is intercalated between the silicate layers resulting in a well ordered multilayer morphology built up with alternating polymeric and inorganic layers. When the silicate layers are completely and uniformly dispersed in a continuous polymer matrix, an exfoliated or delaminated structure is obtained (Fig. 9c). Two complementary techniques are used in order to characterize those structures. XRD is used to identify intercalated structures. In such nanocomposites, the repetitive multilayer structure is well preserved, allowing the interlayer spacing to be determined. The intercalation of the polymer chains usually increases the interlayer spacing, in comparison with the spacing of the organoclay used, leading to a shift of the diffraction peak towards lower angle values (angle and layer spacing values being related through the Bragg's relation: $l.2d \sin y$, where l corresponds to the wave length of the X-ray radiation used in the diffraction experiment, d the spacing between diffractive lattice planes and y is the measured diffraction angle or glancing angle). As far as exfoliated structure is concerned, no more diffraction peaks are visible in the XRD diffractograms either because of a much too large

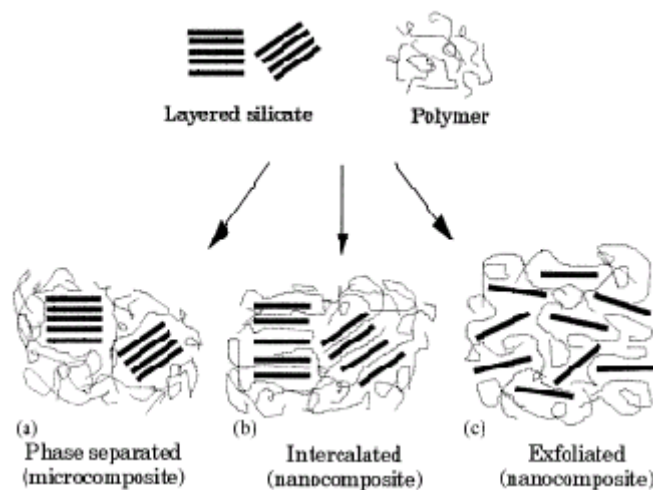


Fig. -9: Scheme of different types of composite arising from the interaction of layered silicates and polymers: (a) phase separated microcomposite; (b) intercalated nanocomposite and (c) exfoliated nanocomposite.

spacing between the layers (i.e. exceeding 8 nm in the case of ordered exfoliated structure) or because the nanocomposite does not present ordering anymore. In the latter case, transmission electronic spectroscopy (TEM) is used to characterize the nanocomposite morphology. Fig. 10 shows the TEM micrographs obtained for an intercalated and an exfoliated nanocomposite.

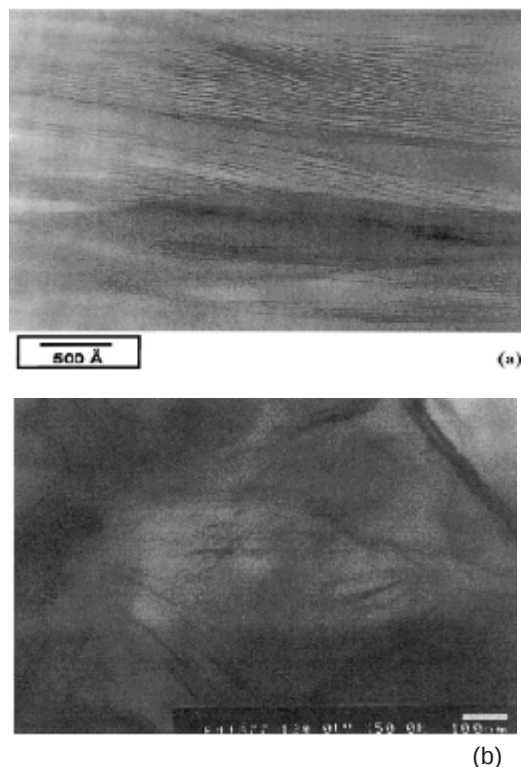


Fig. -10: TEM micrographs of poly(styrene)-based nanocomposites:
(a) intercalated nanocomposite and
(b) exfoliated nanocomposite

Characterization methods

As demonstrated in Fig. 8, the aforementioned characteristics are not completely new. As an ideal form, PNCs are most simple multicomponent systems where: (i) $\langle l \rangle$, the mean distance between nanoparticles (rigid components), is on the order of R_g , the fundamental length scale of the matrix (soft component); and (ii) L , the size of nanoparticle, is also on the order of R_g . Given this idealization and the associated implications, our understanding of established structure-property

relationships developed for traditional composites may not be directly applicable to PNCs. The validity of these relationships and their underlying assumptions are beginning to be reexamined by many researchers in the light of the distinguishing characteristics of PNCs. A wide variety of characterization methods are applied to thoroughly describe the composite morphology and properties. The important aspects of characterization are chemical composition and compositional homogeneity (chemical homogeneity), structure (including crystal system where possible atomic coordinates, bonding and ultra structure) and identification and analysis of defects and impurities influencing the properties of the materials. Characterization, therefore, describes all those features of composition and structure of a material that would suffice for reproducing the material. The advances made in the last few years in characterization techniques, especially in the structure elucidation, have been stupendous and have opened new vistas in solid state materials. Among the several characterization techniques, X-ray diffraction (XRD), scanning electron micrography (SEM) and infrared (IR) spectroscopy are the three important techniques.

X-ray Diffraction

X-ray diffraction¹ has played a central role in identifying and characterizing solids since the early part of this century. 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^{79,80}. X-ray diffraction pattern of amorphous polymer will not show any sharp and highly intensified peaks whereas the nanocomposites of amorphous polymer show sharp and highly intensified peaks. This is due to the development of crystallinity in the amorphous polymer. Figs. 12 (a-b) show the XRD pattern of pure natural rubber and α -Fe₂O₃ dispersed natural rubber composite. Highly intensified peaks occur in the pattern due to the presence of inserted gamma iron oxide materials in the rubber matrix. X-ray diffraction has been most commonly used for routine characterization as well as for detailed structural elucidation. In order to obtain detailed structural

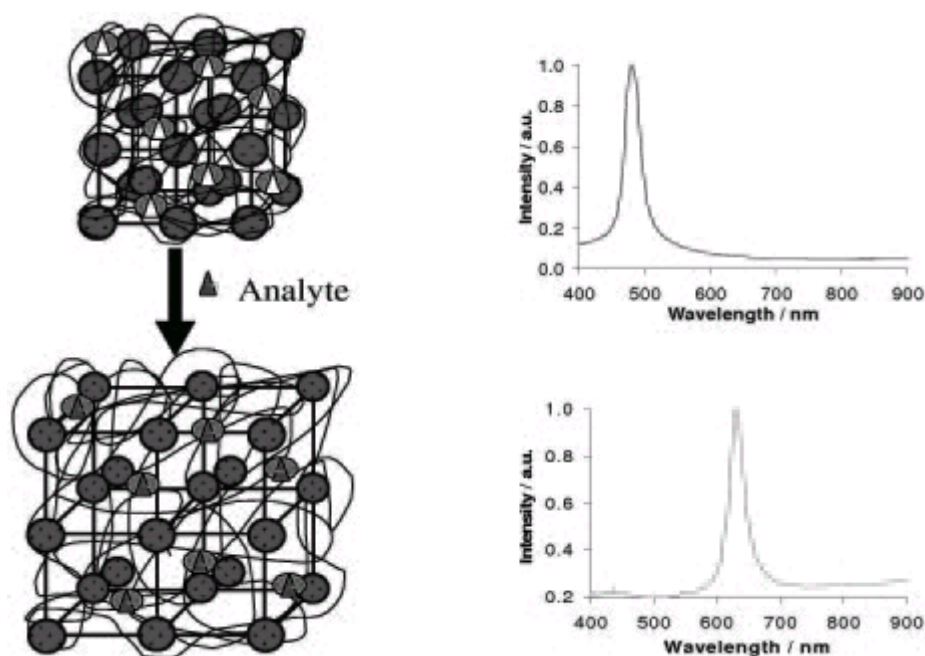


Fig. -11: PCCA photonic crystal sensing materials consist of an embedded CCA surrounded by a polymer hydrogel network that contains a molecular recognition element [101].

information, knowledge of X-ray diffraction intensities is also essential, the intensities being related to the structure factor. Morgan *et al.*⁸¹ made a comparative study of Characterization of Polymer-Layered Silicate (Clay) Nanocomposites by Transmission Electron Microscopy and X-Ray Diffraction. They found that the overall nanoscale dispersion of the clay in the polymer is best described by TEM, especially when mixed morphologies are present. XRD is useful for the measurement of *d*-spacings in intercalated systems but cannot always observe low clay loadings (5%) or be used as a method to identify an exfoliated nanocomposite where no XRD peaks are present (constituting a negative result). Most importantly, the study showed that XRD is not a stand-alone technique, and it should be used in conjunction with TEM⁸².

Scanning Electron Micrograph

Structural phenomena play an important role in determining the properties of a polymer. Mechanical properties are determined not only by the changes in shape conformation and by motion of individual molecules of the polymers, but by the

behavior of larger and more complex structural formations as well. The interface boundaries of these formations, known as super molecular structures, are the sites where chemical reactions in the polymer are most likely to begin and centers of crack formation and incipient destruction are likely to arise. It has been found that extensive occurrences of ordered structures are typical not only of crystalline, but also of amorphous polymers. Despite the complex morphology of structural formation in polymers it should not be forgotten that all these structures are built up of separate polymeric molecules. At a glance it seems self-evident that direct relations must exist between the properties of macromolecules and their ability to form super molecular structures. The shapes of most polymer molecules may vary within wide limits when studying the simplest phenomenon of structure formation. Quite a long time ago it was found that there are two ways by which structures can form. Sufficiently flexible molecules roll up into spherical coil globules, which form in very much the same way as the drops of a liquid under the action of surface tension. But if the macromolecules are sufficiently rigid, the simplest linear structures

result. No separate linear polymer molecules have been observed so far. Evidently in majority of cases, they aggregate into chain bunches usually containing several dozen molecules. The phenomenon of structural transformations occurring during deformation is very typical of polymers. A classic example of structural transformation is the formation of a 'neck' on deformation, described for the case of crystalline polymers some time ago by Kakina. A well-known example is that of poly (methyl methacrylate) where a sharp boundary can be seen between the isotropic and the oriented parts of the specimen. The formation of a 'neck' on deformation of a large spherulite of isotactic poly (methyl methacrylate) takes place and a sharp boundary can be discerned between the unchanged and the oriented portions of a spherulite. In addition, secondary formations can be seen which have resulted from recrystallisation of the oriented parts, and these are also separated by sharp boundary lines. For example, Fig. 13 shows the SEM images of α -Fe₂O₃ dispersed natural rubber composite. From the figure one can observe the fine dispersion of iron oxide particles in the rubber matrix. The dispersed particles have irregular shape and show agglomeration. When studying epoxy filled nanocomposite, Salahuddin *et al.*, with the help of SEM, confirmed that these composite has a special layered structure at all scales and the plane of the layers orients parallel to the surface of the specimen. The uniqueness of this system is this layered structure^{83, 84}.

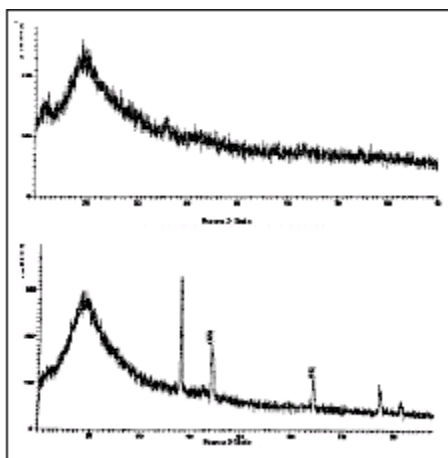


Fig. -12: XRD pattern of (a) pure natural rubber (b) α -Fe₂O₃ dispersed natural rubber.

Infrared Spectroscopy

The shapes of most polymer molecules may vary within wide limits when studying the simplest phenomenon of structure formation. The phenomenon of structural transformations occurring during deformation is very typical of polymers.

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 method can solve many problems in organic chemistry (polymeric materials) and coordination chemistry, and also advantageously complements the results obtained by other 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 frequencies⁸⁵. Infrared (IR) spectroscopy was used to study the surface (by means of external reflection) and the bulk (by means of transmission measurements on micro toned

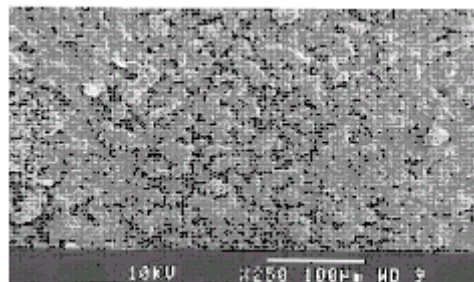


Fig. -13: SEM image of α -Fe₂O₃ dispersed natural rubber.

slices) of specimens obtained by injection molding of a commercial polyamide-6 clay-based nanocomposite material (NCH = nylon clay hybrid) at different mould temperatures and with different part geometries. The ongoing increase in the crystallinity from the surface to the core, in all cases, were confirmed and concluded that both at the surface and in the bulk, the crystalline phase orientation is higher for the NCH than for the PA-6⁸⁶.

Thermal Analysis

Thermal analysis may be defined as the measurement of physical and chemical properties of materials as a function of temperature. The two main thermal analysis techniques are thermogravimetric analysis (TGA) which automatically records the change in weight of a sample as a function of either temperature or time, and the differential thermal analysis (DTA), which measures the difference in temperature, ΔT , between a sample and an inert reference material as a function of temperature; DTA therefore detects change in heat content. A technique closely related but modified to DTA is differential scanning calorimetry (DSC). In DSC, the equipment is designed to allow a quantitative measure of the enthalpy changes, (ΔH), which occurs in a sample as a function of either temperature or time. DSC is an analytical tool which helps to understand the thermal behavior of polymer nanocomposites^{86, 87}. It helps in finding glass transition temperature (T_g) of polymer and its polymer composites. The increase in T_g values shows the presence of inorganic materials in the polymer matrix⁸⁵. TGA-DTA provides quantitative results for the hydration state of the nanocomposites, demonstrates polymer intercalation, and shows that the composites are prepared. Exciting developments can be expected in the area of polymer nanocomposites and structures in the near future. Investigations on polymer nanocomposite can thus pay rich dividends.

Apart from above techniques, several other characterization techniques are being developed according to other nanocomposites properties, they are,

- thermal (enthalpy, thermal capacity, crystallization kinetics)
- thermodynamics (PVT behaviour, equation

of state, gas permeability)

- short- and long-term mechanical behaviour (stress-deformation, fatigue life, fatigue propagation, low-speed impact, durability, fracture behavior)
- surface coverages of the different deposited biomolecules/ enzymes in biosensors can be estimated by means of SPR (Surface plasmon resonance)spectroscopy.
- characterization of the effects of the time-temperature-pressure processing conditions on the microstructure development (orientation, distribution and interaction of nanoclays etc.)

Areas of application

Property improvements have resulted in major interest in nanocomposite materials in numerous biomedical devices, automotive and general/industrial applications.

Sensors represent a most plausible and exciting application area for Polymer nanocomposite field. Logical and promising sensing application areas for polymer nanocomposite nanosensors include medical (e.g., blood gas monitoring/blood analysis, patient monitoring, diagnostic testing), biowarfare detection, genetic analysis, drug screening or discovery, food inspection/testing, environmental monitoring, and industrial chemical process monitoring/leak detection. Nanocomposite nanometer-scale biosensing films, sensitive membrane, biomolecular probes for sensing through spectrometers, thin transducer in biosensors detecting biochemicals through conductivity change are all the miniature devices which are recently made from polymer nanocomposites. Measuring microscopic deflections with sensitive membranes is one of the most versatile approaches for pressure, acoustic, chemical and biomolecular sensing. Some researchers investigated the possibility to improve the properties of some stimuli responsive hydrogels by incorporating clay platelets. The property enhancement, especially on thermal responsivity, swelling-deswelling rate and molecular diffusion, is expected to extend clay-based nanocomposites to such applications as artificial muscles and rapid actuators like as shown in Table 1⁸⁸. Recently, for drug release systems, Messersmith and

Table -1: Potential biomedical and bioengineering applications of clay-based polymer nanocomposites.

Clay/Organoclay	Polymer	Behaviors/Applications	Ref.
MMT	poly(N-isopropylacrylamide)	swelling-deswelling behaviors	39
MMT	polyacrylamide	swelling-deswelling behaviors	90
TDTMA-MMT	poly(N-isopropylacrylamide)	thermal response and controlled release rate	91
Cloisite 20ASomasif-MAE	poly(ethylene-co-vinyl acetate)	drug delivery for dexamethasone	21
Somasif-MAE300			
Cloisite 30BAAPTMA-MMT	poly(N-isopropylacrylamide)	drug release behaviors for caffeine, crystal violet and phenol red	22,23
Halloysite	chitosan/polyethyleneimine	drug release for diltiazem hydrochloride and propranolol hydrochloride	102
Halloysite drug	chitosan/poloxamer 407	delivery for tetracycline	100
MMT	.	drug carrier for 5-fluorouracil	89
MMT	.	iontophoretic delivery for calcium ions	98
DDTMA-Kanemite and its microporous derivative	.	drug loading and release of diphenhydramine hydrochloride	99

Znidarsich³⁹ investigated the feasibility of developing polymer nanocomposites capable of altering their structure and properties upon the application of external stimulus. By *in-situ* polymerization, they synthesized the thermo responsive nanocomposite hydrogels consisting of clay layers dispersed within a poly (N-isopropyl acrylamide) (PNIPAM), a thermally responsive polymer, which exhibits a lower critical solution temperature (LCST) of 32C in the presence of water. The resulting nanocomposite with low loading level of clay (up to 3.5%) showed similar shrinkage behavior to that of pure PNIPAM hydrogel while there was no LCST in the nanocomposite hydrogel with high level of clay (10.7%). In another work, Churochkina *et al.*⁹⁰ reported that the intercalation of negatively charged clay in neutral and slightly charged polyacrylamide matrix improved their mechanical properties while keeping the superabsorbing characteristics of polyacrylamide hydrogel. Later, Liang *et al.*⁹¹ reported a thermosensitive organoclay-PNIPAM nanocomposite with enhanced temperature response which attributed to the improved interfacial chemistry through the coupling agent. Lin *et al.*⁸⁹ attempted to develop a composite as drug carrier and *in-situ* release for colorectal cancer therapy. Such a composite was made by intercalating 5-fluorouracil into the interlayer space of montmorillonite. Asher and his group has developed a novel class of smart optical materials based on soft materials which are responsive to their environment and which can be actuated chemically or photonically (Fig. 11). For this they polymerized crystalline colloidal arrays (CCA), into acrylamide hydrogels and then they functionalized these CCA-embedded hydrogels with dyes and photochromic molecules, as well as with molecular recognition agents which cause the hydrogel to change volume in response to either photons, or the presence of specific analytes (eg Pb²⁺, glucose etc)^{101, 103}.

Gas Barriers

The platelets of filler nanoparticles distributed into a polymer matrix create multiple parallel layers which force gases to flow through the polymer in a "torturous path", forming complex barriers to gases and water vapor. This gaseous barrier property improvement that can result from incorporation of relatively small quantities of nanoclay materials is shown to be substantial. Data

provided from various sources indicates oxygen transmission rates for polyamide-organoclay composites which are usually less than half that of the unmodified polymer. Further data reveals the extent to which both the amount of clay incorporated in the polymer, and the aspect ratio of the filler contributes to overall barrier performance. In particular, aspect ratio is 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. 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 formulations would be expected to enhance considerably the shelf life of many types of food⁹².

Oxygen Barriers

Honeywell have been active in developing a combined active/passive oxygen barrier system for polyamide-6 materials. Passive barrier characteristics are provided by nanoclay particles incorporated via melt processing techniques whilst the active contribution comes from an oxygen scavenging ingredient (undisclosed). Oxygen transmission results reveal substantial benefits provided by nanoclay incorporation in comparison to the base polymer (rates approximately 15-20% of the bulk polymer value, with further benefits provided by the combined active/passive system). Akkapeddi suggests that the increased tortuosity provided by the nanoclay particles essentially slows transmission of oxygen through the composite and drives molecules to the active scavenging species resulting in near zero oxygen transmission for a considerable period of time^{92, 93}.

Food Packaging

Triton Systems and the US Army are conducting further work on barrier performance in a joint investigation. The requirement here is for a non-refrigerated packaging system capable of maintaining food freshness for three years.

Nanoclay polymer composites are currently showing considerable promise for this application. It is likely that excellent gaseous barrier properties exhibited by nanocomposite polymer systems will result in their substantial use as packaging materials in future years⁹³. Mitsubishi Gas Chemical (MGC) and Honeywell Specialty Polymers both are using nanoclays in nylons as barrier layers in multi-layer PET bottles and films for food packaging. MGC's MXD6 nylon nanocomposite, called Imperm N, is used commercially in Europe in multi-layer PET bottles for beer and other alcoholic beverages.

Fuel Tanks

The ability of nanoclay incorporation to reduce solvent transmission through polymers such as polyamides has been demonstrated. Data provided by De Bievre and Nakamura of UBE Industries reveals significant reductions in fuel transmission through polyamide-6/66 polymers by incorporation of a nanoclay filler. As a result, considerable interest is now being shown in these materials as both fuel tank and fuel line components for cars. Of further interest for this type of application, the reduced fuel transmission characteristics are accompanied by significant material cost reductions⁹³. Hyperion Catalysis has introduced nanotubes into other resins used in auto fuel systems, such as modified nylons and fluoropolymers. A new fluoropolymer/nanotube compound is being used to make O-rings for automotive fuel connectors.

Photo Films

The presence of filler incorporation at nano-levels has also been shown to have significant effects on the transparency and haze characteristics of 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 shown to be due to modifications in the crystallisation behaviour brought about by the nanoclay particles; spherulitic domain dimensions being considerably smaller. Similarly, nano-modified polymers have been shown, when employed to coat polymeric transparency materials, to enhance both toughness and hardness of these materials without interfering with light transmission characteristics. An ability to resist high velocity impact combined with

substantially improved abrasion resistance was demonstrated by Haghighat of Triton Systems⁹⁴.

Environmental Protection

Water laden atmospheres have long been regarded as one of the most damaging environments which polymeric materials can encounter. Thus an ability to minimise the extent to which water is absorbed can be a major advantage. Data provided by Beall from Missouri Baptist College indicates the significant extent to which nanoclay incorporation can reduce the extent of water absorption in a polymer. Similar effects have been observed by van Es of DSM with polyamide based nanocomposites. In addition, van Es noted a significant effect of nanoclay aspect ratio on water diffusion characteristics in a polyimide nanocomposite. Specifically, increasing aspect ratio was found to diminish substantially the amount of water absorbed, thus indicating the beneficial effects likely from nanoparticle incorporation in comparison to conventional microparticle loading. Hydrophobic enhancement would clearly promote both improved nanocomposite properties and diminish the extent to which water would be transmitted through to an underlying substrate. Thus applications in which contact with water or moist environments is likely could clearly benefit from materials incorporating nanoclay particles^{95, 96}.

Flammability Reduction

The ability of nanoclay incorporation to reduce the flammability of polymeric materials was a major theme of the paper presented by Gilman of the National Institute of Standards and Technology in the US. In his work Gilman demonstrated the extent to which flammability behaviour could be restricted in polymers such as polypropylene with as little as 2% nanoclay loading. In particular heat release rates, as obtained from cone calorimetry experiments, were found to diminish substantially by nanoclay incorporation. Although conventional microparticle filler incorporation, together with the use of flame retardant and intumescent agents would also minimise flammability behaviour, this is usually accompanied by reductions in various other important properties. With the nanoclay approach, this is usually achieved whilst maintaining or enhancing other properties and characteristics^{96,97}. Germany's Sud-Chemie (U.S. office in Louisville,

Ky.) offers modified nanoclays called Nanofil as flame retardants. It recently developed halogen-free EVA/PE wire and cable compounds containing 3% to 5% of new Nanofil SE 3000 plus 52% to 55% alumina trihydrate or magnesium hydroxide (typically used at 65% levels). The result is said to be improved mechanical properties, smoother cable, and higher extrusion speeds.

Nano-nucleators

Among its many virtues, nanoclay can work as a nucleating agent to control foam cell structure and enhance properties of polymeric foams for applications from insulation to packaging. The University of Toronto's Dept. of Mechanical and Industrial Engineering studied extrusion of chemically foamed LDPE/wood-fiber compounds. Addition of 5% nanoclay to the mix decreased the cell size, increased the cell density and facilitated foam expansion. When burned, the foam showed good char formation. Similar results were obtained in LDPE/nanoclay foam blown with CO₂ gas.

Researchers at Ohio State University's Deptt. of Chemical Engineering (Columbus) found that small amounts of nanoclay surface-grafted with PMMA can reduce cell size and increase cell density in microcellular PS foamed with CO₂. Another OSU study showed that smaller cell size and higher density can be achieved with 5% nanoclay in polyurethane foams blown with pentane or water.

Conclusions

Today, nanocomposites are really nanofilled plastics, where the total internal interfacial area becomes the critical characteristic rather than simply the relative volume fraction of constituents. The use of the moniker nano-'composites' invokes parallels to traditional fiber-reinforced composite technology and the ability to spatially 'engineer, design, and tailored materials performance for a given application. Currently, the realization of 'compositing' PNCs is over the horizon. For the vast majority of investigations, the challenge is still to achieve single-particle dispersions and the subsequent PNCs are treated much as an isotropic, filled polymer. Only recently have examples emerged that consider cost-effective approaches to provide spatial and orientational control of the hierarchical morphology with a precision

comparable to that conventionally obtained through fiber plies and weaving – thus transforming ‘nano-filled systems’ to ‘nanocomposite systems’. In parallel, PNCs are moving beyond commodity plastic applications to critical components of active devices, such as fuel cell membranes, photovoltaics, sensors, and actuators. PNCs have great potential, especially when viewed with respect to the explosion of available functional nanoparticles, enabling never-before-realized properties to be generated within plastics. The underlying framework of PNCs implies that the physics and chemistry of these systems parallels many macromolecular systems, not just filled polymers. The topological similarities between PNCs and other mesoscale polymer systems, such as semicrystalline polymers, block-copolymers, liquid crystals, and colloids, are the impetus for many of these current efforts, providing significant guidance toward understanding the role of processing on structure control and the ultimate impact on properties. Substitution of CNT or other nanomaterials to enhance the performance of current biocompatible materials such as Teflon® , polypropylene and carbon-carbon (C-C) composites is particularly exciting area for near-term commercialization of nanoengineered materials for biomedical applications. Nanostructured filters may be used to prevent blood clot-related deaths due to strokes, heart failure and phlebitis. The high-surface area filter may be implanted in a patient’s circulatory system to break up coagulated blood (precursor to

a clot) and avoid the formation of clots. Other applications that significantly impact the medical devices market include: *facial implants* (currently, C-C structures for facial implant do not allow growth of high-quality tissue; insertion of nanoelements into the structure can modify its surface texture and properties, leading to improved tissue growth); *heart valves* (C-C heart valves have limited useful life due to material chipping; the inclusion of CNT can enhance the valve mechanical strength and durability); *hip and other bone implants* (most hip replacements are made from a polymer, which wears too rapidly to be a lifetime replacement; the inclusion of CNT can increase the material’s strength and lubricity leading to increased comfort and reduced need for replacement). So, is the full realization of PNCs technologically here? No, but it is a viable option today when considering the selection of filled or blend polymer systems. Will PNCs deliver the potential currently ascribed? That is still to be determined, especially since realistic estimates of the ultimate potential, which are based on fundamental understanding of the physics at these scales, are still in development. However, the possibilities are engaging communities worldwide, and the scientific literature is being enriched at an increasing rate with works that show great promise and are beginning to establish a pervasive fundamental understanding of PNC structure-property relationships.

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