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A Review on Nano-composites

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ABSTRACT

Nanocomposites are a class of nanomaterial's wherein one or more phases at nano-sized dimension are embedded in a ceramic, metal, or polymer material. Nanostructure generated by introducing discrete nanoparticles into a continuous solid matrix represents a radical alternative to the structure of conventional particle-reinforced composites. In this article we will discuss about Nanocomposites- structure, classification, method of preparation, applications and its future development. During the past two decades, Nanocomposites have emerged as a new class of materials that received considerable interest in scientific development and engineering applications.

Keywords: Nanomaterial's; Nanostructure; Solid matrix

INTRODUCTION

A Nano-composite is a multiphase material in which, in contrast to micro composites, one of the phases has one, two or three dimension of less than 100nm, or composite phases have Nano scale distances between them. Two materials can be used to fabricate a composite nanomaterial via weak interactions such as vanderwaals, hydrogen bonding and weak electrostatic interactions or by covalent bonds. Nanoparticles, Nano rods, nano fibers and carbon nanotubes (CNTs) are examples of the discrete inorganic units of Nano composite materials.

Multiple components of nano-composites together exhibits synergistic property. The Nanocomposites exhibit multifunctional properties such as high surface to volume ratio for loading of biomolecules such as enzymes, high mechanical strength, high electrical conductivity, redox reactivity and catalytic activity. Nanocomposites are used as transducer materials for enzymes-based bio-Nano electronic devices, imaging targeted drug delivery, detection of cancer cells and pathogens, batteries, gas sensing and artificial implants. The properties of Nanocomposites depends on the dispersion, the larger specific area of nanoparticles will produce a large interfacial area per unit volume between nanoparticle and matrix, which fundamentally differentiates Nanocomposites from conventional composites. Nanocomposites have an estimated annual growth rate of 25% and fastest demand to be in engineering plastics and elastomers. Their prospective is so prominent that they are valuable in numerous areas ranging from packaging to biomedical applications [1].

HISTORY

Nanocomposites were first reported in literature by Blumstein in 1961 and his subsequent studies in 1965 also demonstrated the improved thermal stability of Poly Methyl Methacrylate (PMMA) – layered silicate nanocomposites. The word nanocomposites were coined by Theng in 1970. Nanocomposites were first referenced as early as 1950, and polyamide nanocomposites were reported as early as 1976. However, it was not until Toyota researchers began a detailed examination of polymer/layered silicate clay mineral composites that nanocomposites became more widely studied in both academic and industrial laboratories. In 2009 Azonano explained that true start of polymer nanocomposites history was in 1990 when “Tayota first used clay/nylon-6 nanocomposites for Tayota car in order to produce timing belt covers”.

The aim of the development of nanocomposites is to designate which raw materials and processes are best suited to produce specific nanomaterial by studying their uses, benefits and drawbacks. The history of the usage of nanocomposites is quite old. Egyptian has mixed straws with clay to form bricks. Mongols have used the composites in warfare and even in recent times, during the World War 2, the composites-based materials were used in military appliances, and in the modern era, a large no of composites are used in different fields. Modern nanotechnology truly began in 1981, when the scanning tunneling microscope allowed scientists and engineers to see and manipulate individual atoms. Recently, advances in the ability to characterize, produce and manipulate nanometer-scale materials have led to their increased use as fillers in new types of nanocomposites [2].

STRUCTURE

The structure of nanocomposites usually consists of the matrix material containing the Nano sized reinforcement components in the form of particles, whiskers, fibres, nanotubes, etc. The various equipment’s and techniques like atomic force microscopy (AFM), scanning tunneling microscopy (STM), Fourier transformed infrared microscopy (FTIR), X-ray photoelectron spectroscopy (XPS), nuclear magnetic resonance (NMR), simultaneous small angle X-ray (SAXS), Differential Scanning Calorimetry (DSC), scanning and transmission electron microscopy (SEM/TEM), X-Ray diffractometry (XRD) are used for quantitative characterization of nanostructures and crystalline structures in nanocomposites.

In general the nanoparticle together with the polymer forms the nanocomposites. The nanomaterial’s like nanoparticles, nanotubes, nanofibres, fullerens and nanowires are classified into three types by their geometrics, the three classes are particle, layered, and fibrous material. Carbon black, silica nanoparticles and Polyhedral Oligomeric Silsesquioxanes (POSS) can be classified as nanoparticle reinforcing agents while nanofibres and carbon nanotubes are examples of fibrous materials. When the filler has a nanometer thickness and a high aspect ratio (30-1000) plate-like structure, it is classified as a layered nanomaterial such as organosilicate. The change of length scales from meters (finished woven composite parts), micrometers (fiber diameter), and sub micrometers (fiber/matrix interphase) to nanometers (nanotube diameter) presents tremendous opportunities for innovative approaches in the processing, characterization, and analysis/modeling of this new generation of composite materials [3].

Properties of nanocomposites (3.1)

The properties of the nanocomposites depend upon the clay and polymer combination, the characteristics of the Nano filler and polymer as well as the structure of the composite produced. The optimal structure of nanocomposites for one physical property may not be the best for another physical property.

Mechanical properties (3.1.1)

The surface morphology and the material used for production affects the mechanical properties of nanocomposites, such as tensile strength, elongation and modulus. The improvement of mechanical properties of polymer nanocomposites can be attributed to the good affinity between the polymer and Nano filler along with the high rigidity and high aspect ratio of Nano fillers.

Thermal properties (3.1.2)

The thermal properties of nanocomposites can be analyzed by DSC. From the weight loss on heating the nanocomposites, the thermal stability can be calculated. The heat resistance of nanocomposites on external loading can be measured from the HDT. The dependence of HDT on clay content has been investigated by several researchers. The nanocomposites with good thermal conductivity have multiple applications, such as printed circuit boards, thermal interface materials, heat sinks, connectors and high-performance thermal management system.

Electrical properties (3.1.3)

The electrical properties of nanocomposites depend on several factors, such as aspect ratio, dispersion and alignment of the conductive Nano fillers in the structure. The nanocomposites containing CNTs have superior electrical properties (high energy densities and low driving voltages).The nanocomposites of ether/clay (organically modified) exhibit ionic conductivity that is several orders of magnitude higher than that of the corresponding clay. The electrical conductivity increased by several orders of magnitude with a very small loading (0.1 wt. % or less) of nanotubes to the nanocomposites, without altering other properties such as optical clarity, mechanical properties and low melt flow viscosities. The conductive nanocomposites have found applications in many fields such as electrostatic dissipation, electrostatic painting, electromagnetic interference shielding, printable circuit wiring and transparent conductive coating.

Optical properties (3.1.4)

Titanium dioxide, metal quantum dots and organically modified Nano clays are some of the nanomaterial's that exhibit excellent optical properties for practical applications like solar cells, sensors, coatings etc. The nanomaterial's applied to sensors due to their optical properties like electro-optical sensors, photo luminescent nano sensors, nanostructured surface Plasmon resonance sensors, fiber-optic nano sensors.

Barrier properties (3.1.5)

The nanocomposites have very good barrier property against gases because of their high aspect ratio and by the creation of a tortuous path that retards the progress of the gas molecules through the matrix resin. Inside the nanocomposites structure, the presence of the filler introduces a tortuous path for diffusing penetrants. The permeability is reduced because of the longer diffusive path that the penetrants must travel in the presence of filler. The polyimide nanocomposites containing a small fraction of layered silicate exhibit barrier property against small gases such as oxygen, carbon dioxide, helium, nitrogen and ethyl acetate vapors.

Rheological properties (3.1.6)

The flow behavior of PCL/nylon 6 nanocomposites was significantly different from the corresponding neat matrices. The thermo-rheological properties of the nanocomposites from the behavior of matrices. The viscoelastic properties of nanocomposites are important in relation to composite processing and composite dynamics and microstructure analysis [4].

Factors affecting the properties of nanocomposites (3.1.7)

The factors that affect the functioning of nanocomposites are:

1. Fraction of nanoparticle volume
2. Characteristics of the nanoparticle
3. Shape and size of the embedded material
4. Process used in fabrication of nanocomposites
5. Degree of mixing
6. Formation of aggregates
7. Homogenous dispersion of the two phases
8. Presence of interface between the reinforced material and matrix
9. Interface bonding between the reinforced material and matrix
10. Surface area of nanoparticle
11. Dispersion

CLASSIFICATION

Nanocomposites are classifies into two types: Matrix based and Reinforcement based nanocomposites and they are further classified into various nanocomposites.

Metal/metal nanocomposites (4.1)

Bimetallic nanoparticles will be used in the form of alloy or in the form of shell form will have extensive catalytic and article properties. Metal oxide nanoparticles, nanowires which possess the semiconducting properties are used as fillers gas sensing materials in chemical sensors and biosensors. Semiconductor metal oxides are stable in air; they can be easily dispersed and less expensive.

Metal/ceramic nanocomposites (4.2)

These types of nanocomposites have improved chemical, magnetic, electric and mechanical properties. Metal nanoparticles can be deposited on the ceramic supports by evaporating metal on the selected substrate metal nanoparticles or by dispersion using solvent chemistry. For complex nanocomposites, novel processing techniques such as template synthesis, scanning probe electrochemical methods, electro spinning etc.

Ceramic/ceramic nanocomposites (4.3)

These types of nanocomposites are used in artificial joint implants for fracture failure problems for extending the mobility of patients and eliminating the high cost of surgery. E.g.: zirconia- toughened with alumina.

Polymer based nanocomposites are of the following types (4.4)

Polymer/ceramic nanocomposites (4.4.1)

They contain 1nm thick single ceramic layers of 1nm thick homogenously dispersed to form a continuous matrix. Ceramic layers orient parallel to each other due to their dipole-dipole interaction. Polymer-ceramic nanocomposites are prepared with ceramic Nano powders with the polymer matrices; they have advantages in embedding capacitors as the dielectric constant of ceramic powder is high with highly flexible polymers. Polymer/ceramic nanocomposites (polymer matrices crammed with ceramic Nano powders) are a promising material for embedded capacitors due to their enhanced dielectric constant.

Inorganic/organic polymer nanocomposites (4.4.2)

In these types of nanocomposites, metal clusters of approximately 1-10nm are dispersed into a polymer matrix. The size and structure of the nanocomposites determine the mobility of metal atoms on the polymer surface. For example, in polymethyl methacrylate (PMMA) polymer the cluster size depends on the amount of the cross-linking of the polymer, the mobility of the metal atoms will be based on the crossing linking of the polymer.

Inorganic/organic hybrid nanocomposites (4.4.3)

They are homogenous system with monomers and miscible organic/inorganic components or heterogeneous nanocomposites.

Polymer/layered silicate nanocomposites (4.4.4).

Polymer/layered silicate (PLS) nanocomposites have remarkable properties over virgin polymer and conventional composites.

Polymer/polymer nanocomposites (4.4.5)

Polymers are quite ever struggling to be chip and offered property profiles. The gap between block co-polymer self-assembly and offer nanostructured plastic endowed with still unexplored combinations of properties are becoming narrower. Mixtures of various polymers often phase separate, even when their monomer is mixed homogenously.

Bio-composites (4.4.6)

Metals and metal alloys are used in orthopedics, dentistry and other load bearing applications. Collagen is highly abundant and available in wide varieties.

Carbon nanotube-based nanocomposites (4.4.7)

Due to their mechanical and electrical properties, carbon nanotubes have applications in Nano electronics devices, composites, chemical sensors, biosensors. They are of conductive in nature and their applications are included in the components that require the discharge of the electrostatic potentials. These carbon nanotube-based nanocomposites are electrically conductive and are suitable for applications that require the ability to discharge electrostatic potentials. Carbon nanotubes are of two types i.e., single walled nanotubes (SWNTs) and multiwalled nanotubes (MWNTs) : SWNTs consists of cylindrical single graphite nanostructure sheet, rolled in the form of tube of diameter 1mm to 3nm whereas MWNTs consists of coaxial arrangement of concentric single nanotubes.

Nobel metal-based nanocomposites (4.4.8)

Metal nanoparticles are mixed into polymeric matrix in solution or in the melt form. Porous metal oxides nanocomposites can be easily prepared with tunable porosity, good chemical stability, low-temperature encapsulation, negligible swelling, mechanical and biodegradable stability, high sensitivity at lower operating temperatures for detection of reducing and oxidizing gases [5] **Figure 1.**

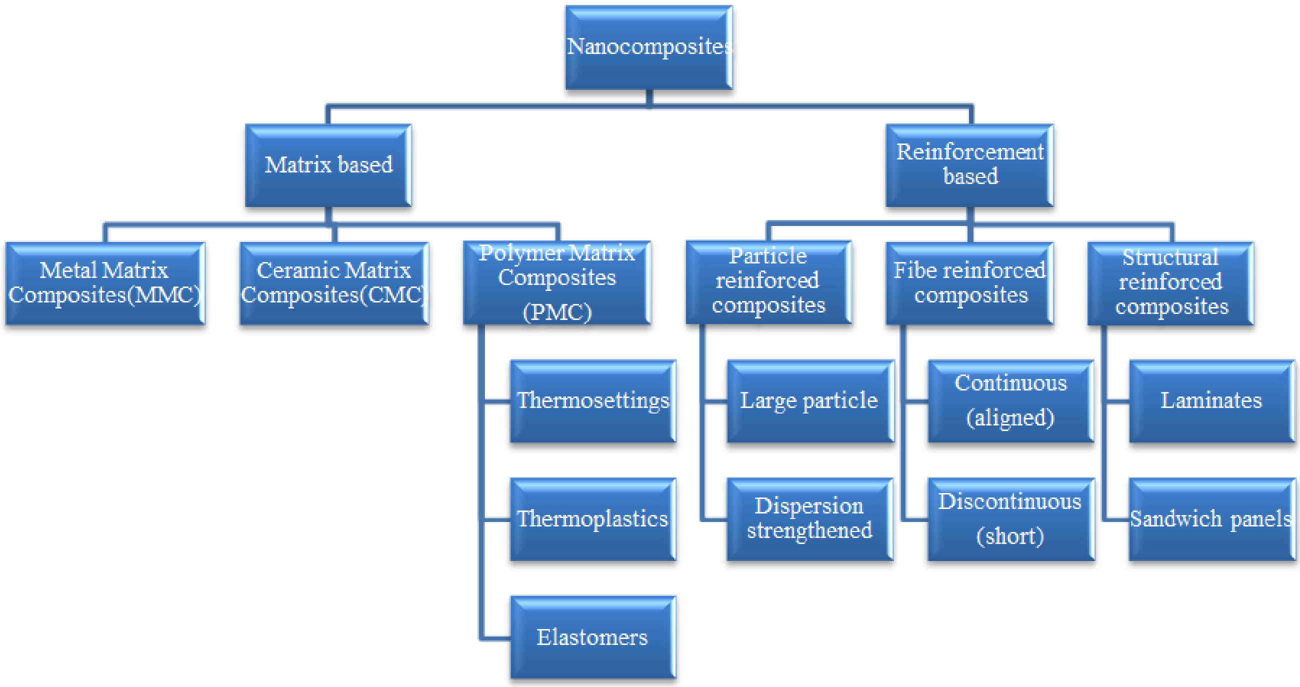

Figure 1. Classification of Nano Composites.

Synthesis of nanocomposites (4.5)

These nanocomposites can be prepared chemically or mechanically. It is of three types (4.5.1) Figure 2.

1. Ceramic matrix nanocomposites (CMNC)
2. Metal nanocomposites (MNC)
3. Polymer nanocomposites (PMNC)

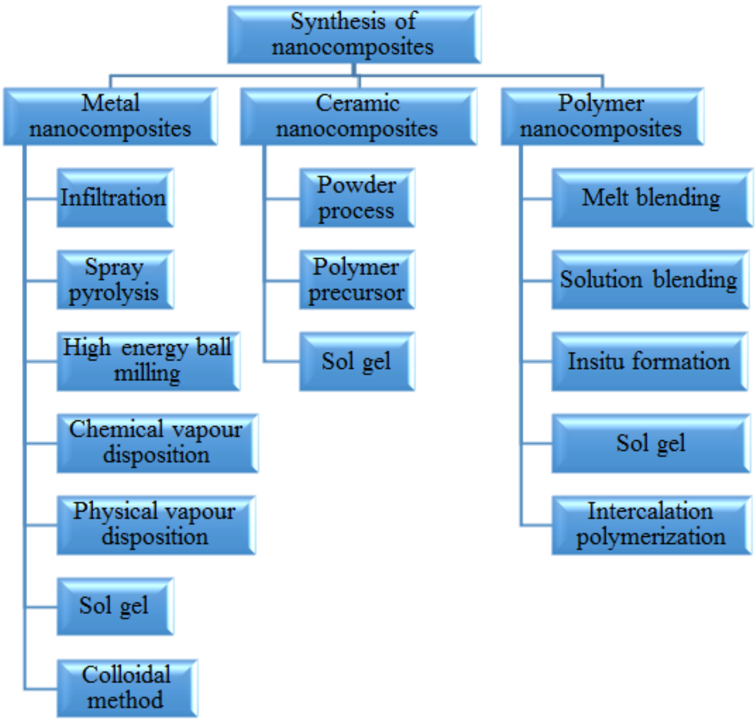

Figure 2. Synthesis of nanocomposites.

1. **Ceramic matrix nanocomposites (CMNC)**

1.1. **Powder process**: Selection of raw materials (mostly powders – small average size, uniformity and high purity) mixing by wet ball milling or attrition milling techniques in organic or aqueous media, drying by heating using lamps and/or ovens, or by freeze drying, consolidation of the solid material by either hot pressing or gas pressure sintering or slip casting or injection moulding and pressure filtration.

- Advantages – simple
- Limitations – low formation rate, high temperature, agglomeration, poor phase dispersion, formation of secondary phases in the product.

1.2. **Polymer precursor process:** Mixing a Si-polymeric precursor with the matrix material, pyrolysis of the mixture using a microwave oven, generating the reinforcing particles.

- Advantages – possibility of preparing final particles ; better reinforcement dispersion
- Limitations – in homogenous and phase-segregated materials due to agglomeration and dispersion of ultra-fine particles.

1.3. **Sol-Gel process:** Hydrolysis and Polycondensation reactions of an organic molecular precursor dissolved in organic media. Reactions lead to the formation of three dimensional polymers containing metal oxygen bonds (sol-gel), drying to get a solid material and further consolidation by thermal treatment.

- Advantages – simple, low processing temperature, versatile, high chemical homogeneity, rigorous stoichiometry control, high purity products, formation of three dimensional polymers containing metal-oxygen bonds. Single or multiple matrices. Applicable specifically for the production of composite materials with liquids or with viscous fluids.
- Limitations – greater shrinkage and lower amount of voids, compared to the mixing method [6]

2. **Metal nanocomposites**

2.1. **Spray pyrolysis**: Dissolution of the inorganic procedures (starting materials) in a suitable solvent to get the liquid source, generation of a mist from this liquid source using an ultra-sonic atomizer, use of a carrier gas to carry the mist into a pre-heated chamber, vaporization of the droplets in the chamber and trapping with a filter, promoting their decomposition to give the respective oxide materials, selective reduction of the metal oxides to produce the respective metallic materials.

- Advantages – effective preparation of ultra-fine, spherical and homogeneous powder in multicomponent systems, reproductive size and quality
- Limitations – high cost associated with producing large quantities of uniform, Nano sized particles

2.2. **Liquid infiltration:** Mixing of fine reinforcement particles with the matrix metal material, thermal treatment, whereby the matrix melts and surrounds the reinforcements by liquid infiltration, further thermal treatment below the matrix melting point, to promote consolidation and eliminate internal porosity.

- Advantages – short contact times between matrix and reinforcements, moulding into different and near net shapes of different stiffness and enhanced wear resistance, rapid solidification, both lab scale and industrial scale production.
- Limitations – use of high temperature, segregation of reinforcements, formation of undesired products during processing.

2.3. **Rapid solidification process(RSP)** : Melting of the metal components together, keeping the melt above the critical line of the miscibility gap between the different components to ensure homogeneity, rapid solidification of the melt by any process, such as melt spinning.

- Advantages – simple, effective.
- Limitations : only metal – metal nanocomposites, induced agglomeration and non-homogenous distribution of fine particles

2.4. **RSP with ultrasonic:** Use of ultrasonic for mixing and for improving wettability between the matrix and the reinforcements.

- Advantages – good distribution without agglomeration, even with fine particles.

2.5. **High energy ball milling:** Milling the powders together till the required Nano sized alloy is obtained, nanocomposites.

- Advantages – homogenous mixing and uniform distribution.

2.6. **CVD/PVD:** PVD-sputtering/evaporation of different components to produce a vapor phase, super saturation of the vapor phase in an inert atmosphere to promote the condensation of metal nanoparticles, consolidation of the nanocomposites by thermal treatment under inert atmosphere. CVD-use of chemical reactions to get vapors of materials, followed by consolidation.

- Advantages – capability to produce highly dense and pure materials, uniform thick films, adhesion at high deposition rates, good reproducibility.
- Limitations – optimization of many parameters, cost, relative complexity.

2.7. Chemical process (sol-gel, colloidal) : Colloidal method-chemical reduction of inorganic salts in solution to synthesize metal particles, consolidation of the dry material, drying and thermal treatment of the resulting solid in the reducing atmosphere, such as H_2, in order to promote selective oxide reduction and generate the metal component.

2.7.1. Sol-gel process-preparation of two micelle solution using mesoporous silica containing 0.1 M $HAuCl_4$ (aq) and 0.6 M $NaBH_4$ (aq), mixing under ultraviolet light till complete reduction of the gold.

2.7.2. For Fe/Au-containing nanocomposites, synthesis of the iron shell, preparation of the second shell and drying of the powders after second gold coating, pressing of the mixture.

- Advantages – simple, low processing temperature, versatile, high chemical homogeneity, rigorous stoichiometry control, high purity products
- Limitations – weak bonding, low wear-resistance, high permeability and difficult control of porosity [7].

3. Polymer Matrix Nanocomposites (PMNC)

3.1. Intercalation/pre polymer from solution: Employed for layered reinforcing material in which the polymer may intercalate. Mostly for layered silicates, with intercalation of the polymer or prepolymer from solution. Use of a solvent in which the polymer or prepolymer is soluble and silicate layers are swellable.

- Advantages – synthesis of intercalated nanocomposites based polymers with low or even polarity. Preparation homogeneous dispersions of the filler
- Limitations – industrial large amounts of solvents.

3.2. In-situ intercalative polymerization: Encasing of the layered silicate within the liquid monomer or a monomer solution, formation of the polymer between the intercalated sheets. Polymerization by the heat or radiation, by diffusion of a suitable initiator or by a catalyst fixed through cation exchange inside the interlayer, before the swelling step.

- Advantages – easy procedure, based on the dispersion of the filler in the polymer precursors.
- Limitations – difficult control intra gallery polymerization.

3.3. Melt intercalation: Annealing of a mixture of the polymer and the layered host above the softening point of the polymer, statically or under shear. Diffusion of polymer chains from the bulk polymer melt in to the galleries between the host layers during the annealing.

- Advantages – environmentally benign, use of polymers not suited for other process, comparable with industrial polymers processes.
- Limitations – limited applications to polyolefin, who represent the majority of used polymers.

3.4. Template synthesis: In-situ formation of the layered structure of the inorganic material in an aqueous solution containing the polymer. The water soluble acts as a template for the formation of layers. Widely used for the synthesis of LDH nanocomposites, but less developed for layered silicates. It is of two types – mixing and in situ polymerization

- Advantages – large scale production, easy procedure.
- Limitations – limited applications, based mainly in water soluble polymers, contaminated by side products.

3.5. Sol-gel process: Embedding of organic molecules and monomers on sol-gel matrices, introduction of organic groups by formation of chemical bonds, in-situ formation of sol-gel matrix within the polymer and/or simultaneous generations of inorganic/organic networks.

- Advantages – simple, low processing temperature, versatile, high chemical homogeneity, rigorous stoichiometry control, high purity products, formation of three dimensional polymers containing metal-oxygen bonds. Single or multiple matrices. Applicable specifically for the production of composite materials with liquids or with viscous fluids.
- Limitations – greater shrinkage and lower amount of voids, compared to the mixing method [8].

APPLICATIONS

Polymer nanocomposites with their unprecedented property combinations and exceptional design possibilities are establishing themselves as high-performance materials of the 21st century and are used in multifarious cutting-edge technologies [9].

Types of polymers used in nanocomposites (5.1)

Vinyl polymer classification (5.1.1)

Methyl methacrylate (MMA), MMA copolymers, polyacrylates, polyaacrylic acid, polyacrylonitrile (AN), polystyrene (S), 4-vinylpyridine, polyacrylamide, polytetrafluoro ethylene, poly(vinyl alcohol), poly(N-vinyl pyrrolidine), poly(vinyl pyrrolidinone), poly(vinyl pyridine), poly(ethylene glycol), poly(ethylene vinyl alcohol), poly(vinylidene fluoride), poly(p-phenylenevinylene), polybenzoxazole, poly(S-co-AN), ethyl vinyl alcohol copolymer, PS-polyisoprene diblock copolymer, other.

Condensation polymer and rubbers classification (5.1.2)

Nylon-6, other polyamides, poly(E-caprolactone) (PCL), poly(ethylene terephthalate) (PET), poly(trimethylene terephthalate), poly(butylene terephthalate), polycarbonate, polyethylene oxide, polyethylene oxide copolymers, poly(ethylene imine), poly (dimethyl siloxane), polybutadiene, polybutadiene, polybutadiene, polybutadiene copolymers, epoxidized natural rubber, epoxy polymer resins, phenolic resins, polyurethanes, polyurethane urea, polyimides, poly(amic acid), polysulphone, polyetherimide, fluoropoly(ether-imide).

Polyolefin classification (5.1.3)

PP, PE, PE oligomers, poly (ethylene-co-vinyl acetate), ethylene propylene diene methylene linkage, poly (1-butene)

1. Specialty polymers: Polypyrrole, poly (N-vinylcarbazole), polyaniline, poly (p-phenylene vinylene), liquid crystalline polymers, hyper branch polymers, cyanate ester, Nafion, Aryl-ethany-terminated imide oligomer.
2. Biodegradable polymers: polylactide (PLA), poly(butylene succinate), PCL, unsaturated polyester, polyhydroxy butyrate, aliphatic polyester **Figure 3.**

Figure 3. Application of nanocomposites.

Future of nanocomposites (5.2)

The number of commercial applications of nanocomposites has been growing at a rapid rate. It has been reported that in less than two years, the worldwide production is estimated to exceed 600,000 tonnes and is set to cover the following areas in the next five to ten years:

1. Drug delivery systems
2. Anti-corrosion barrier coatings
3. UV protection gels
4. Lubricants and scratch free paints
5. New fire-retardant materials
6. New scratch/abrasion resistant materials
7. Superior's strength fibers and films.

Improvements in mechanical property have resulted in major interest in nanocomposites 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. Nanocomposites provides a marked increase in oxygen, carbon dioxide, moisture and odour barrier properties, increased stiffness, strength and heat resistance, and maintains film clarity and impact strength. For the manufacturing industry, these new materials and their commercial applications are coming into focus. Nanotechnology is revolutionizing the world of materials. Although nanocomposites are key applications in numerous industrial fields, a number of key technical and economic barriers exist to widespread commercialization. Biodegradable polymer-based nanocomposites have a great deal of future promise for potential applications as high-performance biodegradable materials. These are entirely new types of materials based on plant and natural materials. Future trends include the extension of this nanotechnology to additional types of polymer system, where the development of new compatibility strategies would likely a prerequisite. There are some safety aspects to be considered while dealing with the nanomaterial, i.e., the release of nanoparticles into the environment is a major health and safety issue. Therefore, studies are essential related to the emission of nanocomposites and their effect on the surroundings, this may be due to the potentially harmful characteristics of nanotechnology products based on their large surface area, crystalline structure and reactivity that may facilitate their easy transport into the environment or interaction with cell constituents, thus intensifying many harmful effects related to their composition [10]

CONCLUSION

This paper discussed about the nanocomposites definition, history, classification, synthesis, properties, polymers used in nanocomposites, applications and the future scope of the nanocomposites. When materials are reduced to Nano sized they display some unusual and exotic properties due to “nano effect”. Nanocomposites are developed to create macroscopic components that have unique physical and mechanical properties. Nano composite-based sensors are expected to possess a serious impact on clinical diagnosis environmental monitoring, security surveillance and ensuring the security of our food. Nanocomposites are suitable materials to meet the emerging demands arising from scientific and technologic advances. Thus, all the three types of nanocomposites provide opportunities and rewards creating new world wide interest in these new materials.

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