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Review Article

POLYMER NANOCOMPOSITES: AN OVERVIEW

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ABSTRACT

A review is presented on the recent developments concerning the concept of Nanocomposites. In This review we particularly focused on basic material used in polymer nanocomposites such as layered silicates, nanotubes and nanofiers, and inorganic material with the properties of these materials used and the application of different polymer nanocomposites particularly in biomedical and pharmaceutical field are discussed here, providing detailed reported in open literature.

Keywords: Polymer nanocomposites, Layered silicates, Nanotubes, Nanofibers, Inorganic polymer nanocomposites.

INTRODUCTION

Nanotechnology can be broadly defined as the creation; processing, characterization and utilization of material devices and system with dimension in the range of 0. 1-100 nm[1]. The new concept of Nanocomposites proposed by Niihara [2]have a new material design and concept which considerably enhanced strength and reasonable development in fracture toughness. Nanocomposites can be made with a improved physical, thermal and other unique properties[3].

The following characteristics of nanocomposites observed by many researchers which are,

(A) Strong change of fracture mode from intergranular fracture of monolithic alumina to transgranular fracture of nanocomposites.

(B) Moderate to considerable improvement in strength.

(C) Enhancement of fracture toughness.

(D) Improvement of several mechanical properties [2, 4].

Polymer-based composites were herald in the 1960s as a new concept for materials [5].

Polymers are attractive as matrix, and several approaches have been reported to incorporate metal nanoparticles into polymers [6]. The synthesis of polymer nanocomposites is generally carried out by the following methods.

a) One is based on insitu polymerization of monomers inside the galleries of the inorganic host[7].
b) The other approach is based on melt intercalation of polymers and it involves annealing a mixture of the polymer and the inorganic host, by dispersing, strong, highly stiff fibres in a polymer matrix[8, 9].

Polymers nanocomposites will supply materials that acquire the ease of processing with significantly improved and even multifunctional properties, opening the way to absolutely new applications of polymers. Polymer-nanoparticle composite whether in solution or in bulk, these materials offer unique mechanical electrical, optical and thermal properties[9]. Techniques used for preparation of polymer nanocomposites are spun polymer fibers with carbon nanofiers as reinforcement. Various techniques are used to dispersion of carbon nanofibers in polymer matrix such as evaporation and sputtering of metallic and organic componants[2]. In general two idealised polymer layered nanocomposite structures are possible intercalated and exfoliated[3]. Commonly used polymers are Polyacrylates, Polystyrene, Polyacrylamide, Polycarbonates, Polyimides, Polysulfone, Polyetherimide etc[10].

In this review we will focus on Basic Materials for Polymer Nanocomposites like Layered Silicates, Carbon Nanotubes and Nanofibers, Inorganic Nanoparticles with applications of different polymer nanocomposites in pharmaceutical field.

Properties of Polymer-Based Nanocomposites

Polymer-based nanoparticle nanocomposites were prepared via a range of processes and shows following mechanical, optical, electrical properties, and thermal properties.

1. Mechanical properties

To get better mechanical properties such as the tensile strength, modulus or stiffness the inorganic material can be added[11]. Though poor compatibility between the polymer matrice and the inorganic particles in nanocomposites prepared by simple physical mixing will produce intrinsic defects which, consequently, result in a harmful effect on the mechanical properties of the nanocomposite.[12]

The mechanical properties of nanocomposites, prepared from various polymers and inorganic particles, did not always enhance. In some cases, the properties of nanocomposites were decrease by the addition of inorganic particles because of aggregation in polymer matrices[13]. To resolve this difficulty, the load amounts of inorganic particles were optimized with organic material.

2. Optical properties

The optical properties of metal nanoparticles consisting of dielectric have long been of concern[14]. The expansion of materials for optical applications with functionality and clearness increases [15]. Polymer-based inorganic nanocomposites show great promise as they can give the necessary stability and easy processability with interesting optical properties. The transparency of these composites depends upon the size and spatial distribution of inorganic particles in the polymer matrix [16].

3. Electrical properties

Nanocomposites are strongly related to the invent of advanced devices for electronic and optoelectronic applications. The dimensional scale for electronic devices has entered the nano-range[17]. The efficacy of polymer/inorganic particle nanocomposites in these areas is quite varied involving many possible applications as well as types of nanocomposites.

4. Thermal properties

For structural application at elevated temperatures, the dimensional constancy of low thermal expansion coefficient of these nanocomposites is also very important [18]. The high thermal expansion coefficient of neat polymers causes dimensional changes during the molding procedure.

Types of polymer Nanocomposites based on basic material used

1] Polymer Nanocomposites based on Layered Silicates

Silicates could absorb catalysts and initiate monomer to make polymer silicates nanocomposites [19]. The polymer adsorption onto the silicates surface plays significant role to affect the diffusion rate of the polymer[20]. Silica coating provides an efficient barrier to quenching of any flurophore by the magnetic cores[21]. Layered silicates are prepared by incorporate finely dispersed layered silicates materials in a polymer matrix. Different approaches can be integrated the ion exchange layered silicates in polymer hosts by in situ polymerization, simple melt mixing or solution intercalation [22, 23]. The use of layered silicates as a immense potential for producing materials considered by enhanced flame retardancy along with better physical properties [24]. Stronger interface between the polymer and silicates clay produces enhanced materials with improved mechanical properties [25]. layered silicates use in the production of nanocomposites are natural or synthetic minerals, consisting of extremely thin layers that are generally bound together with counter-ion[26]. Silica nanoparticles have been widely used at different engineering fields such as biomarker, drug-carrier, nanosensor and nanosized filler because of their biocompatibility and chemical stability [27]. The most commonly used layered silicates are montmorillonite, saponite and hectorite.

Recently, numerous attempts have been made for structural and conformational aspect of polymers in layered silicate based nanocomposites, using techniques such as dynamic light scattering, small angle neutron scattering (SANS), XRD and transmission electron microscopy (TEM)[28].

Properties of polymer Nanocomposites based on Layered Silicates

Nanocomposites consisting of a polymer and layered silicate remarkably enhanced mechanical and materials properties. The main reason for enhancement of properties in nanocomposites is the greater interfacial interaction between the matrix and layered silicate, compared with conventional filler-reinforced systems.

Tensile properties

The tensile modulus of a polymeric material has been revealed to be extremely improved when nanocomposites are formed with layered silicates. N6 nanocomposites prepared through in situ intercalative ring opening polymerization of 1-caprolactam, leading to the formation of exfoliated nanocomposites, show a drastic increase in the tensile properties at quite low filler content. The major cause for the strong improvement in tensile modulus in N6 nanocomposites is the strong interaction between matrix and silicate layers via formation of hydrogen bonds [29].

Heat distortion temperature

Heat distortion temperature (HDT) of a polymeric material is an indicator of heat resistance towards applied load [30].

Thermal stability

The thermal stability of polymeric materials is studied by thermogravimetric analysis (TGA). The weight loss because of the formation of volatile Products after degradation at high temperature is examine as a function of temperature. When the heating occur under an inert gas flow, a non-oxidative degradation occurs and when the air or oxygen is used oxidative degradation of the samples occurs. Commonly, the incorporation of clay into the polymer matrix was found to improve thermal stability by acting as a superior insulator and mass transport barrier to the volatile products generated during decomposition[31].

Optical transparency

Layered silicates are microns in size they are about 1 nm thick. Thus, when single layer is diffuse in a polymer matrix, the resulting nanocomposite is optically clear in visible light[32].

Ionic conductivity

Solvent-free electrolytes are of great interest because of their charge-transport mechanism and their probable applications in electrochemical devices[33].

2] Polymer Nanocomposites based on Nanotubes/Nanofibres

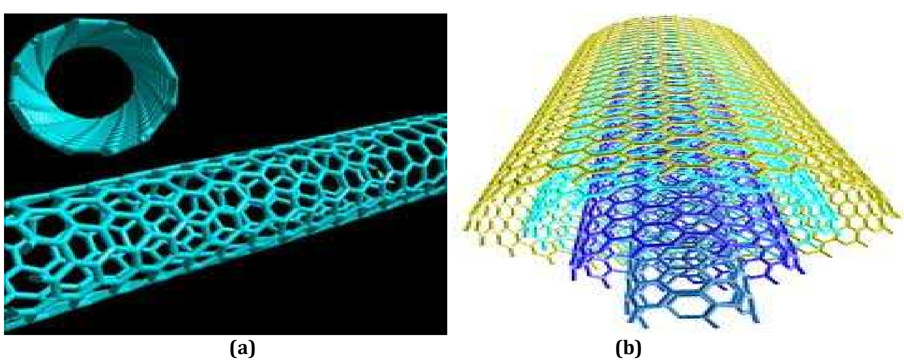
Carbon nanotubes (CNTs) are allotropes of carbon with a cylindrical nanostructure. Nanotubes have been constructing with length-to-diameter ratio of up to 132, 000, 000:1 much larger than for any other material. These cylindrical carbon molecules have properties which are important for nanotechnology, optics, electronics, and other fields of materials science and technology[34]. In particular, due to their extraordinary thermal conductivity, electrical and mechanical properties, carbon nanotubes may find applications as additives to a variety of structural materials.

The development of nanotubes of carbon has involved a major deal of consideration in the last decade since of various attractive properties such as high anisotropy, small dimensions and absorbing tube-like structures. Carbon nanotubes and nanofiers developed by diffusion of carbon (by way of catalytic decomposition of carbon containing gases vaporized carbon from arc discharge or laser ablation) through catalyst and its consequent precipitations as a graphitic filament[35]. The synthesis of nanotubes other than carbon atoms may be possible and they are relatively small, 15-nm-diameter tubes made of molybdenum disulfide and tungsten. Other layered materials synthesized as nanotubes, tube-like forms, had been reported like boron nitride nanotubes with diameters of a few nanometers.

There are three common types of carbon nanotubes which is having high structural perfection. Single-walled nanotubes (SWNTs), Multiwalled nanotubes (MWNTs), Carbon Nanofibers (CNF). consists of a single graphite sheet femalely which is wrapped into a cylindrical tube. Single-walled carbon nanotubes (SWNTs) which show a range of remarkable mechanical and electronic properties because of their unique structure and dimensions [36]. Multiwalled nanotubes (MWNTs) which comprise of an group of such nanotubes that are concentrically nested like rings of a tree trunk [37]. Single–walled carbon nanotubes (SWNTs) reveal a range of remarkable physical, electronic, mechanical properties because of their unique structure and dimensions. Carbon nanotube has commercial interest because of their conductivity at very low loading levels [38].

Morphology of Single-walled nanotubes (SWNTs) and Multiwalled nanotubes (MWNTs)

The morphology of nanotubes shows a high degree of variability. Variability includes the nanotube length, diameter, chirality and tube-end configuration [1]. SWNTs and MWNTs are usually made by carbon-arc discharge, laser ablation of carbon, or chemical vapor deposition [39]. Diameter of SWNTs ranges from 0.4 to >3 nm. and the diameter of MWNTs ranges from 1.4 to at least 100 nm.[40]



(a) (b)

Fig. 1: a) Single-walled carbon nanotubes[41] b) Multiwalled carbon nanotubes[42]

Nanotubes sheets, fibers and composites should retain the properties of individual nanotubes as for as possible. Both SWNTs and MWNTs are used for reinforcing thermoset polymer (epoxy, phenolic and polyimide) as well as (polypropylene, polystyrene, poly methyl methacrylate (PMMA), nylon 12 and poly ether ether ketone (PEEK).

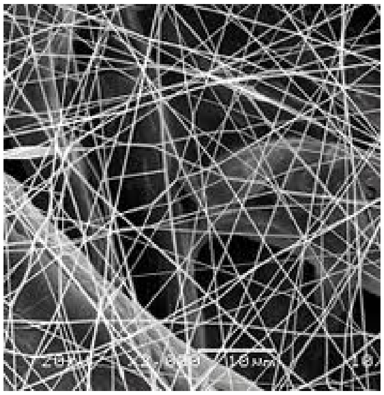


Fig. 2: Nanofibre[43]

Ogasawara et al [44] reinforced a phenylethyl terminated polyimide with MWNTs, which are a few hundred mm in length and diameter range upto 20-100 nm. The composite were made by mechanical blending of nanotubes in matrix. The modification of nanotube surface by the formation of covalent chemical bonds between nanotubes and polymer matrix, and enhances their interaction and gives rise to higher interfacial shear strength than van der waals bonds.

Properties of Nanotubes/Nanofibres

The properties of CNT are important to understand for designing composite materials Properties of nanotubes and nanostructured materials are discussed as follows

Elastic and thermal properties

Nanotubes are the stiffest known fiber[45]. The tensile strength is ranges upto 50 GPa or above [46]. When compared with carbon reinforcing fibers, the strength to weight ratio of nanotubes in the axial direction is up to four times greater. The greatest strain of SWNT is 10%, which is superior than most structural materials. These strong mechanical properties are due to the C–C covalent bonding and the seamless hexagonal network. Thermal conductivity is also very high in the direction of the nanotube axis, typically about 1750–5800 W/mK.

Electrical conductivity

Electronically, the carbon nanotube can be metallic or semiconducting, depending on the chirality. Carbon nanotubes also have been predicted to conduct current ballistic ally without dissipating heat. Metallic SWNT behave as long ballistic quantum conductors with the charge carriers and it has the strongest electrochemical properties perhaps because the lower resistance allow a greater double layer charge buildup[47].

Magnetoresistance

The CNT also have spin-dependent transport properties or magnetoresistance. The direction of magnetization of the ferromagnetic electrodes used to contact the nanotube, defines the spin direction of the charge carriers into and out of the nanotube and a change in the resistivity of the nanotube. The nanotube-metallic junction appears to have a strong effect on the spin-dependent transport [48].

Piezoresistance

A pioneering experiment shows that the conductance of a metallic CNT might decrease by orders of magnitude when strained by an atomic force microscope tip. It appears that the band structure of a carbon nanotube is dramatically changed by mechanical strain and that the conductance of the CNT can increase or decrease depending on the chirality of the nanotube [49].

Electrokinetics of nanotubes

The electrical properties (conductivity and dielectric constant) of a nanotube are generally different than of the fluid. Therefore, when a nanotube is in an electrolyte, it will attract ions of opposite electrical polarity forming an electrical double layer [50].

3] Polymer Nanocomposites based on Inorganic Material

Polymeric composites consisting of inorganic nanoparticles and organic polymers represent a new class of materials, which enhance performance compare with their micro-particle counterparts [51]. Polymer-inorganic nanocomposite materials are inorganic nanofiller dispersed at a nanometer level in a polymer matrix [52]. The inorganic particles provides mechanical and thermal stability, and new functionalities that depend on the chemical nature, the structure, the size, and crystallinity of the inorganic nanoparticles (silica, transition metal oxides, , nanoclays, metallic phosphates, metal chalcogenides and nanometals) the inorganic particles can execute or get better mechanical, thermal, magnetic, electronic properties, density and refractive index, etc[53].

Methods for the preparation of polymer-based inorganic nanoparticles composites

Various methods are used for preparation of polymer based inorganic nanocomposites. The important ones are:

(i) Intercalation of nanoparticles with the polymer or pre-polymer from solution [32].
(ii) In situ intercalative polymerization [54].
(iii) Melt intercalation[55].
(iv) Direct mixture of polymer and particulates [56].
(v) Template synthesis[57].
(vi) *In situ* polymerization[58].
(vii) Sol-gel process[59].

The most important one is possibly the incorporation of inorganic nanoparticles in polymers. Polymer based nanocomposite synthesis affected by inorganic particles size, content, molecular weight and properties of inorganic particles.

Maleic anhydride (MA) grafted polyethylene/clay nanocomposites were prepared by simple melt compounding [45]. The exfoliation and intercalation behaviors depended on the hydrophilicity of polyethylene grafted with maleic anhydride and the chain length of organic modifier in the clay. When polyethylene has a higher grafting level of MA than the critical grafting level of MA (0. 1 wt %) and the number of methylene groups in alkylamine chain has more than 16, polyethylene/clay nanocomposites are completely exfoliated.

Applications of Polymer Nanocomposite

Nanocomposites are of huge interest to biomedical technologies such as controlled drug delivery, tissue engineering, dental applications, and bone replacement/ repair. some biopolymers commonly used in biomedical applications.

1. Hydroxyapatite (HAP)–polymer nanocomposites is used as a biocompatible and osteoconductive substitute for bone repair and implantation [60].
2. Collagen-basedis polypeptidic gelatine most widely used in wound dressings and pharmaceutical adhesives in clinics [61].
3. Polysaccharides like alginate provide a natural polymeric sponge structure that is used in tissue-engineering scaffold design [62].
4. Composite membranes from HAP nanoparticles and chitosan/collagen sols have also been synthesized to study connective-tissue reactions[63].
5. Studies of the nucleation of calcium phosphates and bone cell signalling used acidic macromolecules as the nanocomposite matrix. Specially amino acids like aspartic acid and glutamic acid are used as the matrix protein. Both of these amino acids

are play an important role in intercellular communication and osteoblast differentiation that increases extracellular mineralization [64].

6. Aliphatic polyesters used as the major choice for materials in degradable drug delivery systems[65].
7. The polyesters are used in biomedical fields, poly (L-lactic acid) (PLLA) is the most widely used [66].
8. PLLA has general applications in drug delivery devices, scaffolds, sutures, prosthetics, bone screws, vascular grafts for temporary internal fixation [67].
9. Montmorillonite Clay (MMT) in a PLLA solution are used to improve mechanical and biodegradation characteristics and ideal pore sizes (microns) for blood vessel invasion, cell growth, and nano-sized pores for nutrient/waste transfer [68].
10. The use of organically modified layered silicates predominantly attractive among for biocompatibility and mechanical properties [69].
11. Quantaum dots (QD) can be treated with drug moieties for instance, non-steroidal anti-inflammatory drugs, in order to specifically target certain organ or cell organelles [66].
12. The nanoparticle size plays an significant role in determining the magnetic response of the materials and hence influence its biomedical activity [70].
13. Nanocomposites can be used as agent in nanomedicine, for example one of the most promising application is a bimodal anticancer therapy, encompassing photodynamic and hyperthermic capabilities [71].
14. Applications of magnetic-flurecent nanoparticles is in cell tracking, diagnostic, cytometry, magnetic separation and to treat various diseases[71].

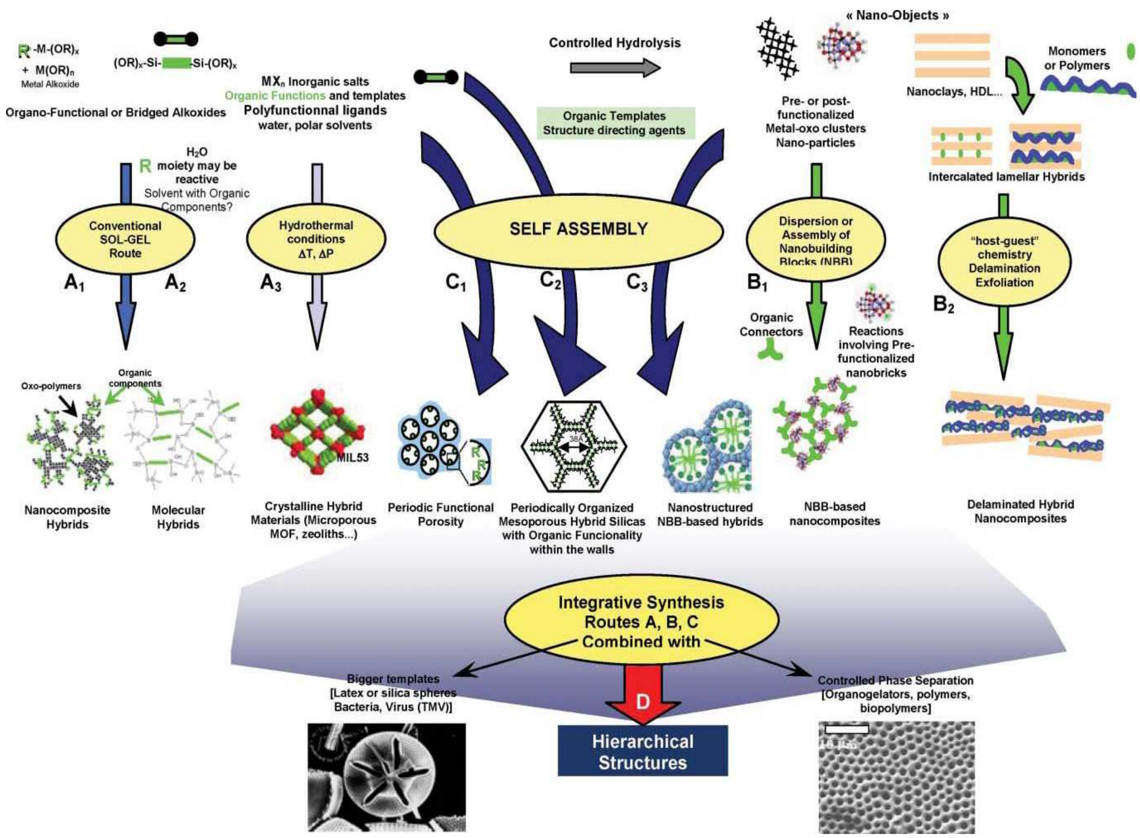


Fig. 2: Schematic representation of the main chemical routes for the synthesis of polymer-inorganic nancomposites. Path A: sol-gel process; Path B: assembly or dispersion; Path C: self-assembly procedures; Path D: integrative synthesis [16].

CONCLUSION

This review reports on the basic materials used in polymer nanocomposites properties and application in pharmaceutical field. A layered silicate shows properties such as tensile properties, thermal stability. In recent years nanotubes and nanofibers shows excellent properties such asmechanical strength and toughness, they are considered a promising reinforcing material. Various different polymers are recently used in pharmacy field for the development in tissue engineering, controlled drug delivery, bone replacement/repair, dental application.

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