



Polymer Nanocomposites: Progress In Synthesis, Characterization, And Use

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Abstract

Polymeric nanocomposites, combining organic polymers and inorganic nanoparticles, are emerging as high-performance materials with vast applications across various fields including biomedical, environmental, and energy sectors. These hybrid materials offer superior mechanical, electroactive, and thermal properties due to the synergistic interaction between the polymer matrix and the nanoparticles. Despite their potential, challenges such as nanoparticle dispersion within the polymer matrix need to be addressed to enable commercial-scale production. Various synthesis methods, including sol-gel, in situ intercalative polymerization, and in situ polymerization, have been developed to achieve well-dispersed nanocomposites. This study explores the classification, properties, and diverse applications of polymer nanocomposites, highlighting their potential in sectors like aerospace, automotive, civil infrastructure, food packaging, energy, and biomedical fields. By addressing the current limitations and optimizing synthesis methods, polymeric nanocomposites can significantly advance technology and material science, offering innovative solutions to contemporary challenges.

Keywords: Polymer nanocomposites, In situ polymerization, Sol-gel process, Hybrid nanomaterials, Synthesis

INTRODUCTION

Polymeric nanocomposites are of great importance in different fields. Synthesis of hybrid nanocomposites based on organic (polymer) and inorganic components has gained serious attention of researchers due to their extensive range of applications in biomedical, environment, and energy-related areas. Progress in polymer science has created an opportunity to produce an extensive range of materials having superior mechanical, electroactive, and thermal properties. In addition to this direction of developing new nanocomposites, researchers are continuously exploring novel techniques to prepare hybrid nano-materials by combining desirable features of polymers and nanoparticles. In literature, various challenges have been mentioned in preparing polymeric nanocomposites with desired features. The major limitation for producing nanocomposites at a commercial scale is the absence of economical methods for nanoparticle dispersion into the polymer matrix. The aggregation of nanomaterials hinders its benefits associated to the dimension (nanoscale), and hence, well-dispersed and isolated nanoparticles within the polymer matrix are needed. Hence, there is a need to develop synthesis methods that are effective on nanoscale yet appropriate for macroscopic processing. Researchers have developed a range of synthesis methods for preparing polymer nanocomposites which include direct processing, in situ polymerization, sol-gel, etc.

Polymer Nanocomposites

Polymer nanocomposites (PNCs) are a new class of reinforced hybrid materials that are formed by the dispersion of nanoscale clay particles throughout a polymer matrix. PNCs is an appropriate synonym for nanoparticles in the form of rods, spheres, or sheets dispersed within the polymer matrix, has aroused tremendous interest, both in academia and industry. Nanocomposites consist of an organic polymer matrix embedded with inorganic particles, which have at least one of the dimensions in the nano range. The particles may be spherical (metallic or ceramic), fibrillar (CNT) or lamellar. The polymer nanocomposites combine the concept of both composites and nanomaterials. Though nanocomposite can include porous media, colloids, gels and copolymers, mainly it is considered to mean the solid combination of nano-dimensional phases differing in properties due to dissimilarities in structure and

chemistry. There is the presence of nanocomposite in nature, such as the structure of abalone shell, tooth, nacre and bone.

The technology of nanocomposites involves the use of very small amount of Nanofillers. The addition of nanofillers can strongly impact the macroscopic properties of the polymer nanocomposite. The properties of nanocomposites are quite superior to conventional composites as nanoscale organic-inorganic materials are mixed on a nearly molecular level in the former.

7.2 Classification of polymer nanocomposites

Three types morphologies are possible for polymer nanocomposite depending on the degree of NPs separation. These three possible types include conventional composites, intercalated nanocomposites and exfoliated nanocomposites. In traditional composites also called microcomposites, the polymer is incapable to be intercalated between the fillers layers and thus a composite having separated phases is normally obtained. In intercalated type polymer nanocomposites, a single extended polymeric chain is well intercalated between the filler layers, which results in a well-arranged multi-layer morphology having intercalated layers of the polymer and fillers. When the fillers layers are uniformly and completely dispersed in a continuous polymeric matrix result in the formation of an exfoliated nanocomposite. In intercalated polymer nano-composites, the nano-fillers keeps their crystallographic structures original. However, the distance between the sheets, interlayers or planes is greater than original state because as the nano-fillers are intercalated within the polymer chains and produce sandwich-like structure. There is maximum reinforcement of nano-fillers in the exfoliated nanocomposites owing to the large contact of surface area between the NPs and matrix. In this type the original structures of nano-fillers get lost as the disorder arrangement is found in the polymeric matrix. The interfacial interactions within the polymeric chains and nano-fillers are much more in exfoliated polymer nanocomposites as compared to the intercalated nano-composites.

Depending on nano-fillers dimension, polymer nanocomposites are classified in zero-dimensional, one-dimensional and two-dimensional polymer nanocomposites. The examples of zero-dimensional nanomaterials are spherical nanoparticles of metals (Au, Ag, Cu, Fe etc.) and metal oxides (Fe₂O₃, CuO, ZnO, TiO₂ etc.) and quantum dots (CdS, CdSe, SnTe, ZnS etc.). The examples of one-dimensional nanomaterials includes carbon nanofibers, carbon nanotubes, polyaniline nanofibers, cellulose nanofibers and nano whiskers. Similarly layered silicates, nanoclay and graphene-based materials are the most widely investigated two-dimensional nanomaterials. Similarly depending on the thermal response of polymers utilized, polymer nanocomposites are categorized into thermosetting and thermoplastic polymer nano-composites. Polymers nanocomposites are also classified on the basis of class of polymers utilized such as polyester nano-composites, polyurethane nano-composites, polyamide nano-composites, polyether nano-composites, polycarbonate nano-composites, silicone polymer nanocomposites, polyacrylate nano-composites, diene polymer nanocomposites, olefinic polymer nano-composites, cellulosic nano-composites etc

LITERATURE REVIEW

Bhattacharya et al. (2008) provides a comprehensive examination of polymeric nanocomposites, discussing their synthesis, characterization, and applications. The authors emphasize the importance of the interaction between the polymer matrix and the nanoparticles, which significantly influences the overall properties of the nanocomposites. They also explore various methods of nanocomposite preparation, including in situ polymerization, melt blending, and solution blending, each with its distinct advantages and challenges.

Fu et al. (2019) offer a critical review of some basic aspects of polymer nanocomposites, highlighting their unique properties such as improved mechanical strength, thermal stability, and barrier properties. The authors delve into the fundamental mechanisms that underpin these enhancements, including the role of interfacial interactions, nanoparticle dispersion, and

the polymer matrix's crystallinity. They also discuss the various types of nanoparticles used, such as clays, carbon nanotubes, and metal oxides, and their specific contributions to the nanocomposite properties.

Winey and Vaia (2007) provide insights into the structural and property relationships of polymer nanocomposites. Their work focuses on the role of nanoparticle dispersion and distribution within the polymer matrix, which are critical for achieving the desired properties. They explore various techniques for characterizing nanocomposite structures, including electron microscopy, X-ray scattering, and spectroscopy. The authors also discuss the potential applications of polymer nanocomposites in fields such as automotive, aerospace, and electronics, where enhanced material properties are crucial.

Azad and Mohsennia (2020) present a novel application of polymeric nanocomposites in environmental remediation. They describe the development of a free-standing polyvinyl butyral-polyacrylonitrile/ZnAl-layered double hydroxide nanocomposite membrane designed for the removal of heavy metals from wastewater. The study demonstrates the nanocomposite membrane's high efficiency in removing contaminants, attributing this to the synergistic effect of the polymer matrix and the layered double hydroxide nanoparticles. This work highlights the potential of polymer nanocomposites in addressing environmental challenges through innovative material design.

John (2020) explores the use of polymer nanocomposite-based electrochemical sensors and biosensors. The author reviews the advancements in sensor technology facilitated by the incorporation of nanocomposites, which offer enhanced sensitivity, selectivity, and stability. The integration of various nanoparticles, such as metal oxides, carbon nanotubes, and conductive polymers, into the sensor matrix is discussed, along with their impact on the sensor's performance. The potential applications of these sensors in medical diagnostics, environmental monitoring, and food safety are also highlighted.

SYNTHESIS METHODS

A polymeric particle polymer nanocomposite contains a rigid polymer component dispersed within a flexible polymer matrix on a nanoscale level. The rigid polymer, with high modulus and high strength, usually has high melting temperature, is insoluble in organic solvents, and combining it with the flexible polymer is thermodynamically unfavourable. Therefore, it is very difficult to prepare a nanocomposite, and phases may undergo segregation during processing and end use. Hydrodynamic effects and physico- or chemi-sorption of matrix at filler surface governs the reinforcement.

Nanocomposites are prepared mainly by three methods:

3.1 Sol-gel process

This includes two approaches: hydrolysis of the metal alkoxides and then polycondensation of the hydrolysed intermediates. This process provides a method for the preparation of inorganic metal oxides under mild conditions starting from organic metal alkoxides, halides, esters etc. Sanchez and coworkers controlled the polymerisation rate and stresses in metal alkoxides through the concept of chemically controlled condensation, where competitive esterification reactions were used to slow the elimination of water. In addition to the manipulation of the processing parameters, another approach toward dealing with the stress associated with drying involves the modification of the inorganic metal oxide with an appropriately functionalised polymer. Such inorganic-organic hybrids or composites can be designed to offer a range of properties depending on the relative composition of each component, size scale of phase separation, and reactivity between the components.

3.2 In-situ intercalative polymerisation

This is a good method for the preparation of polymer clay mineral hybrids. A novel class of fillers is anisotropic layered silicates of the montmorillonite type, which can be modified by cation exchange with organic ammonium salts, thus producing organophilic clays, further called organoclays. Organophilic modification affords compatibility between filler and polymer. Different methods have been introduced to achieve matrix-filler compatibilization:

melt or solution intercalation of organoclay with polymers, cation exchange of montmorillonite with polymers bearing quaternary ammonium groups, or cation exchange and subsequent polymerisation with monomers containing quaternary ammonium groups. These compatibilization techniques account for improved interfacial adhesion and effective dispersion of either intercalated silicate layer aggregates or even individual exfoliated silicate layers. Such nanocomposites exhibit superior stiffness, impact, strength and heat distortion temperature.

3.3 In-situ polymerisation

In this method, nanometre scale inorganic fillers or reinforcements are dispersed in the monomer first. This is then polymerised using a technique similar to bulk polymerisation. Krishnamoorti and Giannelis prepared an important class of polymer layered silicate nanocomposites by this method. The endtethered polymer layered silicate nanocomposites were prepared by in-situ polymerisation of ϵ -caprolactone. For this the silicate surface was converted from a hydrophilic to an organophilic surface by an ion exchange of the metal cations by 12-aminolauric acids. The carboxyl groups of the aminolauric acid initiate the polymerisation of the monomer and the polymerisation proceeds via a ring opening of the ϵ -caprolactone.

4. Properties of nanocomposites

The properties of the nanocomposite depend upon the clay and polymer combination, the characteristics of the nanofiller and polymer as well as the structure of the composite produced. The nanocomposite possesses noticeable differences in their thermal, mechanical, barrier and electrical properties when compared with traditional composites.

The optimal structure of a nanocomposite for one physical property may not be the best for another physical property. This section highlights the properties of nanocomposites.

Thermal Properties:

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

Mechanical Properties:

The mechanical properties of nanocomposites, such as tensile strength, elongation and modulus, are affected by the surface morphology and the material used for production. The improvement of mechanical properties of polymer nanocomposite can be attributed to the good affinity between the polymer and nanofiller along with the high rigidity and high aspect ratio of nanofillers.

Electrical Properties:

The electrical properties of nanocomposites depend on several factors, such as aspect ratio, dispersion and alignment of the conductive nanofillers in the structure. The nanocomposites containing CNTs have superior electrical properties (high energy densities and low driving voltages). The nanocomposite 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 nanocomposite, without altering other properties such as optical clarity, mechanical properties and low melt flow viscosities. The conductive nanocomposite has found applications in many fields such as electrostatic dissipation, electrostatic painting, electromagnetic interference shielding, printable circuit wiring and transparent conductive coating.



Barrier Properties:

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 nanocomposite 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 nanocomposite containing a small fraction of layered silicate exhibit barrier property against small gases such as oxygen, carbon dioxide, helium, nitrogen and ethyl acetate vapours.

Rheological Properties:

The flow behavior of PCL / nylon 6 nanocomposite was significantly different from the corresponding neat matrices. The thermo-rheological properties of the nanocomposite from the behavior of matrices. The viscoelastic properties of nanocomposites are important in relation to composite processing and composite dynamics and microstructure analysis. Krishnamoorti and Giannelis (1997) were the first to describe the rheological properties of in situ polymerized nanocomposite with end-tethered polymer chains.

APPLICATION OF NANOCOMPOSITES

Polymer nanocomposites with their unprecedented property combinations and exceptional design possibilities are establishing themselves as high-performance materials of the twenty-first century and are used in multifarious cutting-edge technologies. A few of the applications of nanocomposites are briefly discussed here.

Aerospace:

Projecting heavy lift systems to the earth's lower atmosphere incurs a huge cost in terms of fuel prices. The fuel cost amounts to about 30% of the operational cost even in general aviation. So the implementation of polymer/CNT nanocomposite in a space shuttle and commercial aircraft such as Boeing 787 and Airbus A380.

Automotive:

With increasing global concerns for low fuel economy and low emissions in the case of land transportation systems, research is trending toward the low cost, high performance, and lightweight polymer nanocomposite. This class of novel materials is expected to increase the speed of production, environmental and thermal stability, and recyclability, while reducing the weight.

Infrastructures/Civil Structures:

Polymer composites with nanofillers have always acted as game-changers about their use in structural components (buildings, bridges, and other engineered structures) which can be attributed to the high strength-to-weight ratio of the class of materials. They are also highly durable in terms of thermal, mechanical, and barrier properties. One of the important components of civil structures is concrete. But a lot of improvements are expected in it concerning its increased durability, tensile strength, and reduced brittleness. Composites with organo-clays are commonly used as barrier coatings to protect the civil structures against environmental aging and corrosion. A coating based on epoxy polymer with nano-ceramic fillers could shield the concrete structures from UV radiations, contamination, and deterioration.

Food Packaging:

Polymer nanocomposites, owing to their superior functionality, antibacterial properties, lightweight, and cheap and simple processing techniques, have proved to be better replacements for the conventional packaging materials such as metals, ceramics, and paper. The inherent barrier properties (mechanical and thermal), biodegradability, self-healing, and self-cleaning of those composites increase the shelf life of the packaged food items. Polymer/clay has considerable performance in the packaging of processed foods like cheese, meats, confectionary, cereals, boil-in-bag foods, and even for fruit juices and carbonated drinks.

Energy:

Materials with high dielectric constant, optimum piezoelectric properties are often searched for their importance in energy storage and harvesting application. Low dielectric constant polymers, when blended with dielectric / piezoelectric ceramics nanofillers, form a good combination with requisite properties. Flexible polymer-based nanocomposite suitable for energy harvesting serve as the new generation functional materials.

Bio-Medical:

Polymer nanocomposites form the basic building blocks of life systems starting right from bone (a combination of ceramic phosphate crystallites and collagen fibers forming strong and dense cortical bone or spongy shear resistant cancellous bone), teeth (enamel, cementum, and dentin containing different volume fractions of hydroxyapatite crystals along with collagenous or non-collagenous proteins), or wood (consisting of cellulose and lignin). Hence, polymers blended with other nanoparticles open up great avenues for a multitude of applications in a biomedical field such as tissue engineering, bone replacement/repair, dental applications, controlled drug delivery, and many more. Several magnetic polymer nanocomposite have been used in biomedical and environmental applications.

CONCLUSION

In conclusion, the synthesis, characterization, and application of polymer nanocomposites represent a significant advancement in materials science, offering a versatile platform for enhancing the properties of conventional polymers through the incorporation of nanoscale fillers. The development of novel synthesis techniques, such as sol-gel processes, in-situ intercalative polymerization, and in-situ polymerization, has enabled the creation of nanocomposites with superior mechanical, thermal, electrical, and barrier properties. These enhanced materials have demonstrated their potential across a wide range of applications, including aerospace, automotive, infrastructure, food packaging, energy, and biomedical fields. However, the commercialization of these nanocomposites faces challenges related to nanoparticle dispersion and economic feasibility, necessitating further research to optimize synthesis methods and achieve large-scale production.

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