

A STUDY OF ORGANIC/INORGANIC HYBRID NANOCOMPOSITES

RAI SUJEET AKHILESH

RESEARCH SCHOLAR, DR.K.N. MODI, UNIVERSITY NEWAI, RAJASTHAN

DR. MOHAMMAD SHAHID

ASSISTANT PROFESSOR DR.K.N. MODI, UNIVERSITY NEWAI, RAJASTHAN

ABSTRACT

The synthesis and characterization of organic and inorganic hybrid nanoparticles assembly represent a cutting-edge area of research at the interface of chemistry, materials science, and nanotechnology. This abstract provides an overview of recent advancements and key findings in this field, encompassing various synthesis methods and characterization techniques employed to understand the structure, properties, and applications of hybrid nanoparticle assemblies. The synthesis of organic and inorganic hybrid nanoparticles involves the integration of organic molecules or polymers with inorganic nanoparticles, resulting in hybrid structures with unique properties and functionalities. Several synthesis approaches have been developed, including in situ polymerization, surface functionalization, and self-assembly techniques. These methods offer precise control over the composition, size, shape, and surface chemistry of hybrid nanoparticles, enabling tailored design for specific applications.

KEYWORDS: Organic/Inorganic, Hybrid Nano composites, cutting-edge area, specific applications, synthesis methods

INTRODUCTION

The field of polymer Nano composite materials has had the attention, imagination, and close scrutiny of scientists and engineers in recent years. This scrutiny results from the simple premise that, using building blocks with dimensions in the nanoscale makes it possible to design and create new materials with unprecedented

flexibility and improvements in their properties. Nanocomposites could open up a large window of opportunity to overcome the limitations of traditional micro-meter scale polymer composites, in which the filler is <100 nm in at least one dimension [1, 2]. There are several reasons for the widely accepted state of polymer nanocomposites. First, unprecedented combinations of properties have been

observed in a few polymer nanocomposites [3]. For example, the inclusion of equi-axed nanoparticles in thermoplastics, and particularly in semi crystalline thermoplastics, increases the yield stress, the tensile strength, and Young's modulus [4] compared to pure polymer. A second reason for the large increase in research and development efforts was the discovery of carbon nanotubes in the early 1990s [5]. Third, significant development in the chemical processing of nanoparticles and the in situ processing of nanocomposites has lead to unmatched control over the morphology of such composites. It has also created an almost unlimited ability to control the interface between the matrix and the filler.

The most obvious difference between micro and nano composites is the small size of the fillers. For example, very small nanoparticles do not scatter light significantly, and thus it is possible to make composites with altered electrical or mechanical properties that retain their optical clarity. In addition, the small size means that, the particles do not create large stress concentrations and thus do not compromise the strength of the polymer. A similar concept applies for electrical breakdown strength. In addition to the effect of particle size on properties, the

small size of fillers leads to an exceptionally large interfacial area in the composites [5]. Figure 1.1 shows the particle size dependence of the interface at various filler concentrations. The increase in interfacial area below 100 nm is dramatic. With a 5 vol% particle added in a polymer, the 10 nm particles will result in 40 vol% interfaces. The 5 nm particles result in 95 vol% interface of the composites. When the fillers are spheroid, more complicated filler-matrix interaction and physical properties are to be expected, which requires more investigations.

Factors Affecting Properties of PMCs

Interfacial Adhesion

The behaviour of a composite material is explained on the basis of the combined behaviour of the reinforcing element, polymer matrix, and the filler/matrix interface. To attain superior mechanical properties the interfacial adhesion should be strong. Matrix molecules can be anchored to the filler surface by chemical reaction or adsorption, which determines the extent of interfacial adhesion. The developments in atomic force microscopy (AFM) and nano indentation devices have facilitated the investigation of the interface.

Size, Shape and Orientation of Dispersed Phase Inclusions (Particles, Flakes, Fibers, and Laminates)

Particles have no preferred directions and are mainly used to improve properties or lower the cost of isotropic materials [7]. The shape of the reinforcing particles can be spherical, cubic, platelet, or regular or irregular geometry. Particulate reinforcements have dimensions that are approximately equal in all directions. Large particle and dispersion-strengthened composites are the two subclasses of particle-reinforced composites. A laminar composite is composed of two dimensional sheets or panels, which have a preferred high strength direction as found in wood. The layers are stacked and subsequently cemented together so that the orientation of the high strength direction varies with each successive layer [8].

Low dimensional fillers are more difficult to disperse than their three dimensional cousins. The difference arises because three-dimensional quasi spherical particles touch at a point, where as one dimensional rods or tubes can contact along a line, thus leading to enhanced particle interaction. Two-dimensional sheets offer even larger contact area [9].

Properties of the Matrix

Properties of different polymers will determine the application to which it is appropriate. The chief advantages of polymers as matrix are low cost, easy processability, good chemical resistance, and low specific gravity. On the other hand, low strength, low modulus, and low operating temperatures limit their use [10]. Varieties of polymers for composites are thermoplastic polymers, thermosetting polymers, elastomers, and their blends.

The lack lustre performance of nanocomposites has been attributed to a number of factors including poor dispersion, poor interfacial load transfer, process-related deficiencies, poor alignment, poor load transfer to the interior of filler bundles, and the fractal nature of filler clusters [11]. Even well dispersed nanofillers naturally aggregate to form clusters, whose size extent to length scales exceeding 1 μm . The large scale aggregated character of nanoscale fillers is the most important factor that compromises nanocomposites' mechanical performance. Unless the aggregation is limited, interface modification, improved processing, more rigorous dispersion, higher native aspect ratio, and better morphology control will not lead to the lofty performance improvements once predicted [12].

ORGANIC/INORGANIC HYBRID NANOCOMPOSITES

When inorganic phases in organic/inorganic composites become nanosized, they are called hybrid nanocomposites. Organic/inorganic nanocomposites are generally organic polymer composites with inorganic nanoscale building blocks. They combine the advantages of the inorganic material (e.g., rigidity, thermal stability) and the organic polymer (e.g., flexibility, dielectric response, ductility, and processability) [13]. The inorganic particles not only provide mechanical and thermal stability, but also impart new functionalities that depend on chemical nature, structure, size, and crystallinity of the inorganic nanoparticles (silica, transition metal oxides, metallic phosphates, nano clays, nano metals and metal chalcogenides). Indeed, the inorganic particles can implement or improve mechanical, thermal, electric, magnetic and redox properties, density, refractive index, etc. [14]. Inorganic nanoscale building blocks include nanotubes, layered silicates (e.g., montmorillonite, saponite), nanoparticles of metals (e.g., Au, Ag), metal oxides (e.g., ZnO, TiO₂, Al₂O₃), semiconductors (e.g., PbS, CdS) etc. In fact, among the numerous inorganic/organic nanocomposites,

polymer/silica composites are the most commonly reported in the literature [15].

Organic polymer-based inorganic nanoparticle composites have attracted increasing attention because of their unique properties emerging from the combination of organic and inorganic hybrid materials. Generally, the resultant nanocomposites display enhanced optical, mechanical, magnetic and optoelectronic properties. Therefore, the composites have been widely used in the various fields such as military equipments, safety, protective garments, automotive, aerospace, electronics and optical devices. However, these application areas continuously demand additional properties and functions such as high mechanical properties, flame retardation, chemical resistance, UV resistance, electrical conductivity, environmental stability, water repellence, magnetic field resistance, radar absorption, etc. Moreover, the effective properties of the composites are dependent upon the properties of constituents, the volume fraction of components, shape and arrangement of inclusions and interfacial interaction between matrix and inclusion [16]. One method to facilitate dispersion of nanoparticles is to coat the inorganic nanoparticle with a thin layer of polymer to introduce steric stabilization [17]. By

coating the nanoparticle with a thin layer of polymer [18-19] and surface functionalization of the nanoparticles [20-21], the van der Waals influence from the nanoparticles can be masked and the compatibility between the hosting organic polymer and inorganic nanoparticle can be improved, thereby facilitating better nanoparticle dispersion and increased loading amount.

Polymer/Inorganic Filler Interactions

Nanocomposites have at least an order of magnitude more interfacial area than traditional composites. This increase in interfacial area results in a 3D interfacial region within the polymer matrix that can have properties significantly different from those of the bulk polymer. The local chemistry, chain mobility, chain conformation, and degree of chain ordering or crystallinity can all vary continuously from the filler/matrix boundary to some point in the polymer bulk.

The nanofiller surface/polymer interactions greatly influence the glass transition temperature (mobility, relaxation spectra). The presence of attractive surface of nanoparticle, decrease the polymer chain mobility and thus increase the T_g of the system [28]. The glass transition temperature of a bulk part can be raised or

lowered by the addition of nanoparticles [29]. Ash et al. [30] have shown that, for non-wetting nanoparticle/polymer composites (Alumina/PMMA), the glass transition temperature starts to decrease at a specific filler volume fraction corresponding to an inter-particle distance of about 200 nm.

Modification of Interfaces

Literature on the modification of interfaces of traditional composite fillers is extensive. Many of the methods, however, are not directly applicable to nanocomposites for several reasons. Carbon and glass fibers are usually coated as long fibers on a spool, which is not practical for nanofibers. In addition, methods that require drying the particles are not appropriate for metal oxide and metal nanoparticles, because during drying (even at only 100 °C), they may agglomerate significantly. Freez drying methods are more appropriate.

Modification of Inorganic Nanoparticles

A review by Caruso [43] provides extensive background on the modification of nanoparticle surface. The author cites two primary methods for modifying an inorganic nanoparticle surface with organic molecules. The first requires connecting a short chain molecule such as siloxane onto

the surface through grafting or strong hydrogen bonding. The second involves application of a coating by polymerizing a polymer onto the nanoparticle. In addition, inorganic coatings can be applied.

POLYMER/FILLER HYBRID ASSEMBLING AND INTERACTIONS

Effect of Nanofillers on Crystallization

In addition to homogeneous dispersion of fillers, strong interfacial adhesion between polymer matrix and filler is essentially crucial to obtain high-performance polymer/filler composites. Interfacial crystallization offers a possible means to enhance polymer/filler interfacial interaction in composite systems composed of semicrystalline polymer and filler. That is through the enhanced interaction between polymer and filler caused by the crystallization of polymer on the filler surface. These filler particles can act as nuclei and induce the polymer lamellae grow on the filler surface. These as-formed crystalline superstructures are generally denoted as 'hybrid crystalline structure' or 'hybrid crystal', in contrast to conventional supermolecular crystalline structures consisting of only polymer species [142].

Effect of Nanofillers on Polymer Chain Dynamics

It is known that there is a rigid amorphous fraction (RAF) in semicrystalline polymers. The RAF exists at the interface of crystal and amorphous phase as a result of the immobilization of a polymer chain due to the crystal. Also, the RAF fraction sometimes exists at the surface of nanoparticles in the polymer nanocomposites material. However, unlike semicrystalline polymers, the silica nanoparticle does not undergo any transition at the temperature when RAF devitrifies.

TERNARY HYBRID NANOCOMPOSITES

To prepare high-performance hybrid composites, the dispersion of inorganic fillers and the interfacial interaction between matrix and fillers are considered as the key issues. The filler/matrix interfacial cohesion directly influences the interfacial stress transfer in the composites structures, thereby significantly affects the integrated mechanical properties [181-184]. The major challenge faced by these hybrid nanocomposites is the incompatibility between the organic polymer and inorganic filler and as a result, the strong tendency of aggregation of nanoparticles [185-186]. Surface treatment on nanoparticles can reduce the degree of aggregation to some

extent [187]. Even the surface treatment has not been fully succeed in avoiding the strong aggregation tendency of nanoparticles and thus their negative effect on properties at higher filler loadings due to the dominant filler-filler interaction over filler-matrix interaction. Very recently, hybrid ternary systems, having two nanoscale materials were found very promising in enhancing the dispersion level of nanoparticles [188-189]. The super microstructure development associated with the synergism between the nanofillers leads to enhanced properties [190-191].

Hybrid Effect

Hybrid reinforcements for polymer composites are getting acceptance because they offer a range of properties that cannot be obtained with a single type of reinforcement. Two different filler types are used in the case of three-component compounding, which produces so called hybrid structures, in which, properties of different components are combined [192]. Hybridisation with more than one filler type in the same matrix provides another dimension to the potential versatility to the parent system. Properties of the hybrid composite may not follow a direct consideration of the independent properties of the individual components. A positive or

negative hybrid effect can be defined as a positive or negative deviation of a certain property from the rule of mixture behaviour [193]. Recent investigations on composites having multi component filler systems have focused mainly on thermoplastics and thermosets. Superior mechanical and dynamic mechanical properties can be acquired by the synergistic effect of two filler types. Such synergistic interactions result in a unique micro structural development that ultimately influences the properties especially the mechanical behaviour of composites that contain both particles [194]. Depending on the shapes of the materials and the way they are combined, changes in morphology and microstructure is expected. Additionally, the use of hybrid system is expected to improve the dispersion by eliminating the tendency of aggregation by the difference in surface characteristics of two kinds of nanoparticles [195].

Selection Criteria for Hybrid Fillers

It is mainly based on the dimensionality of the filler in nano level. Low dimensional fillers are more difficult to disperse than their three dimensional cousins. The difference arises, because three dimensional quasi spherical particles touch at a point, whereas two dimensional layered

silicates have less contact area that exists naturally as stacks [196]. At the same time, both the systems are not free from the problem of aggregation. The combination of two and three dimensional filler types may synergistically act one another and produce a system with more efficient dispersion. This selection criterion favours the hybridisation of spherical nanofillers and clay platelets [197].

CONCLUSION

The synthesis and characterization of organic-inorganic hybrid nanoparticles will be crucial to address pressing challenges and unlock transformative applications. The need for this research will stem from the increasing demand for advanced materials with tailored properties for diverse fields. In medicine, the development of hybrid nanoparticles will revolutionize drug delivery and imaging, enhancing treatment efficacy. Furthermore, in catalysis and environmental remediation, the unique features of these nanoparticles will hold the potential to improve reaction rates and facilitate sustainable solutions. The study will be crucial for understanding the synergistic effects between organic and inorganic components, enabling the design of customized nanoparticles with enhanced performance. By addressing these needs,

this research will contribute to the ongoing evolution of nanotechnology, fostering innovation and offering practical solutions to complex problems in various industries.

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