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Nanocomposites – An Overview

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Abstract:- The definition of nanocomposites 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. This research presents a detailed definition of nanocomposites, its origin, classification, properties, benefits, as well as its future. With the proper choice of compatibilizing chemistries, the nanometer-sized clay platelets interact with polymers in unique ways. The paper shows that the application possibilities for packaging include food and non-food films and rigid containers. In the engineering plastics arena, a host of automotive and industrial components can be considered, making use of lightweight, impact, scratch-resistant and higher heat distortion performance characteristics. In plastics the advantages of nanocomposites over conventional ones don't stop at strength. The high heat resistance and low flammability of some nanocomposites also make them good choices to use as insulators and wire coverings.

Keywords:- Nanocomposites, nanoparticles, biomineralization, nanomer, polymer.

I. INTRODUCTION

Dimensionality plays a critical role in determining the properties of matter. The nanostructure of a material is the key factor in the development of novel properties and in controlling the structure at the nano-level. Nanotechnology is therefore a highly promising field of the twenty-first century, which is expected to totally restructure the technological applications in the fields of semiconductors, inorganic, as well as organic materials, energy storage, and biotechnology.

The term "nanotechnology" can be defined as the controlled manipulation of materials with at least one dimension less than 100 nm. This technology attempts to integrate chemistry, physics, materials science, and biology to create new material properties that can be exploited to develop facile processes for the production of electronic devices, biomedical products, high performance materials and consumer articles. The commercialization of nanotechnology is expected to boost wide technological development, improve quality of life and societal benefits around the world.

The definition of nano-composite material has over the years 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. According to Azonano (2009) nanocomposites are "materials with a nanoscale structure that improve the macroscopic properties of products." He observed that typically, nanocomposites are clay, carbon, or polymer, or a combination of these materials with nanoparticle building blocks.

The general class of nanocomposite organic/inorganic materials is a fast growing area of research. Significant effort is focused on the ability to obtain control of the nanoscale structures via innovative synthetic approaches. The properties of nanocomposite materials depend not only on the properties of their individual parents but also on their morphology and interfacial characteristics.

This rapidly expanding field is generating many exciting new materials with novel properties. The latter can derive by combining properties from the parent constituents into a single material. There is also the possibility of new properties which are unknown in the parent constituent materials. Nanocomposites can then be defined as nanomaterials that combine one or more separate components in order to obtain the best properties of each component (composite). In nanocomposite, nanoparticles (clay, metal, carbon nanotubes) act as fillers in a matrix, usually polymer matrix.

Kamigaito (1994) defined nanocomposite as a multiphase solid material where one of the phases has one, two or three dimensions of less than 100 nanometers (nm), or structures having nano-scale repeat distances between the different phases that make up the material. The mechanical, electrical, thermal, optical, electrochemical, catalytic properties of the nanocomposite will differ markedly from that of the component materials.

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 $(Mo_3Se_3\text{-})_n$ 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, non-linear optics, battery cathodes and ionics, nano-wires, sensors and other systems.

The general class of organic/inorganic nanocomposites may also be of relevance to issues of bio-ceramics and biomineralization in which in-situ growth and polymerization of biopolymer and inorganic matrix is occurring. Finally, lamellar nanocomposites represent an extreme case of a composite in which interface interactions between the two phases are maximized. By judiciously engineering the polymer-host interactions, nanocomposites may be produced with a broad range of properties.

Inorganic layered materials exist in great variety. They possess well defined, ordered intralamellar space potentially accessible by foreign species. This ability enables them to act as matrices or hosts for polymers, yielding interesting hybrid nano-composite materials.

Lamellar nano-composites can be divided into two distinct classes, intercalated and exfoliated. In the former, the polymer chains alternate with the inorganic layers in a fixed compositional ratio and have a well defined number of polymer layers in the intralamellar space. In exfoliated nano-composites the number of polymer chains between the layers is almost continuously variable and the layers stand >100 Å apart. The intercalated nano-composites are also more compound-like because of the fixed polymer/layer ratio, and they are interesting for their electronic and charge transport properties. On the other hand, exfoliated nano-composites are more interesting for their superior mechanical properties.

In his work, Maniar (2004) observed that a significant amount of industrial and governmental research is being conducted on nanocomposites. He pointed out that the most popular polymers for research and development of nanocomposites are polyamides, polypropylene, polyethylene, styrenics, vinyls, polycarbonates, epoxies, acrylics, polybutylene terephthalate, and polyurethanes as well as a variety of miscellaneous engineering resins. However, the most common filler is montmorillonite clay; these nanoclays are unique since they have a platy structure with a unit thickness of one nanometer or less and an aspect ratio in the 1000:1 range. Unusually low loading levels are required for property improvement.

Expected benefits from nanocomposites include improvement in modulus, flexural strength, heat distortion temperature, barrier properties, and other benefits and, unlike typical mineral reinforced systems, they are without the conventional trade-offs in impact and clarity.

II. HISTORY OF NANOCOMPOSTES

Nanocomposites have been studied for nearly 50 years, but few references address the importance of how the organoclay is processed into the plastic of choice. 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.

Acquarulo & O'Neil (2002) in their work observed that in the early 1980s that Toyota's Central Research and Development Laboratories began working with polymer-layered silicate-clay mineral composites and that the period was when the technology began to be studied more widely. The clay mineral that is generating the most interest for use in nanocomposites is montmorillonite, generically referred to as nanoclay, and sometimes referred to as bentonite.

According to Briell (2004) bentonite "is natural clay that is most commonly formed by the in situ alteration of volcanic ash or by the hydrothermal alteration of volcanic rocks" This clay is widely available and relatively inexpensive, thus becoming the most widely used clay in nanocomposite applications.

In his study, Azonano (2009) explained that the true start of polymer nanocomposites history was in 1990 when "Toyota first used clay/nylon-6 nanocomposites for Toyota car in order to produce timing belt covers." He pointed out that after that other automotive application was implemented, which include:

- Mitsubishi´s GDI cover clay/nylon-6 nanocomposites engines; and
- General Motors clay/polyolefin nanocomposites step assistant GMC Safari and Chevrolet Astro vans.

However, Nanocomposites have been used commercially since Toyota introduced the first polymer/clay auto parts as the potential applications go beyond automotive industry. One of the most promising is drink packaging application considering increased barrier properties of polymer clay nanocomposites. It is easy to understand the commercial and technical importance of this field. 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.

III. PREPARATION OF NANOCOMPOSITES

In their study, Zapata etal (2008) explained that the preparation of nanocomposites can be done by three routes, which are “solution blending, the molten state, and in situ polymerization.” They pointed out that the latter consists in placing the monomer and the catalyst between the clay layers, and polymerization takes place in the gap, so as polymerization progresses the spacing between the clay's layers increases gradually and the dispersion state of the clays changes from intercalated (the ordered of layered silicate gallery is retained) to exfoliated (delamination with destruction of the clay sheet order). The advantages of this method are 1) the one step synthesis of the metallocene polymer nanocomposites; 2) improved compatibility of the clay and the polymer matrix; and 3) enhanced clay dispersity.

Nanocomposites can also be prepared by dispersing a Nanomer nanoclay into a host polymer, generally at less than 5wt% levels. This process is also termed exfoliation. When a nanoclay is substantially dispersed it is said to be exfoliated. Exfoliation is facilitated by surface compatibilization chemistry, which expands the nanoclay platelets to the point where individual platelets can be separated from another by mechanical shear or heat of polymerization. Nanocomposites can be created using both thermoplastic and thermoset polymers, and the specific compatibilization chemistries designed and employed are necessarily a function of the host polymer's unique chemical and physical characteristics. In some cases, the final nanocomposite will be prepared in the reactor during the polymerization stage. For other polymer systems, processes have been developed to incorporate Nanomer nanoclays into a hot-melt compounding operation. Figure 1 shows a Nanomer particles protruding from a plasma-etched polymer matrix.

Figure 1: Nanomer particles protruding from a plasma-etched polymer matrix. Source: Nanocor

The first step in the preparation of the nanoclay involves purifying approximately 99 percent of the montmorillonite. The second step involves surface treatment of the clay. According to Capanescu & Capanescu (2002), montmorillonite is hydrophilic and relatively incompatible with most hydrophobic polymers, so it must be chemically modified to make its surface more receptive to dispersion. After the clays are chemically treated, they are dispersed in the polymer. In his study DeGaspari (2001), observed that the clays are incorporated into the polymer matrix by one of two approaches: during polymerization or by melt compounding (This is the difficult part of the technology and may limit the use of nanocomposites. The dispersion process requires a custom solution for each polymer used, so developing polymer nanocomposites becomes a capital intensive research and development project. According to Nanoparticle News (2003), very few compounding firms have this kind of capability, and this leaves resin producers or well-funded startup companies to develop these materials.

In general, nanocomposites exhibit gains in barrier, flame resistance, structural, and thermal properties yet without significant loss in impact or clarity. Because of the nanometer-sized dimensions of the individual platelets in one direction, exfoliated Nanomer nanoclays are transparent in most polymer systems. However, with surface dimensions extending to one micron, the tightly bound structure in a polymer matrix is impermeable to gases and liquids, and offers superior barrier properties over the neat polymer. Nanocomposites also demonstrate enhanced fire resistant properties and are finding increasing use in engineering plastics.

Nanomer nanoclays provide plastics product development teams with exciting new polymer enhancement and modification options. With the proper choice of compatibilizing chemistries, the nanometer-sized clay platelets interact with polymers in unique ways. Application possibilities for packaging include food and non-food films and rigid containers. In the engineering plastics arena, a host of automotive and industrial components can be considered, making use of lightweight, impact, scratch-resistant and higher heat distortion performance characteristics.

IV. CLASSIFICATION OF NANOCOMPOSITES

The general class of nanocomposite organic/inorganic materials is a fast growing area of research. Significant effort is focused on the ability to obtain control of the nanoscale structures via innovative synthetic approaches. The properties of nanocomposite materials depend not only on the properties of their individual parents, but also on their morphology and interfacial characteristics.

Cammarata (2006) pointed out that "most nanocomposites that have been developed and that have demonstrated technological importance have been composed of two phases, and can be microstructurally classified in three principal types: (a) Nanolayered composites composed of alternating layers of nanoscale dimension; (b) nanofilamentory composites composed of a matrix with embedded (and generally aligned) nanoscale diameter filaments; (c) nanoparticulate composites composed of a matrix with embedded nanoscale particles."

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There are basically two modes of classification for nanocomposites. They are the organic and inorganic nanocomposites. So many efforts are taken by the researchers to take control over nanostructures by synthetic approaches. The properties of the nanocomposites not only depend upon the individual parent compositions but also on their morphology and interfacial characteristic.

In the classification of the nanocomposites the inorganic components can be 3 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 (Mo3Se3-)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, non-linear optics, battery cathodes and ionics, nanowires, sensors and other systems.

The general class of organic/inorganic nanocomposites may also be of relevance to issues of bio-ceramics and biomineralization, in which in-situ growth and polymerization of biopolymer and inorganic matrix is occurring. Finally, lamellar nanocomposites represent an extreme case of a composite in which interface interactions between the two phases are maximized.

However, Theng (1979) explained that nanocomposites can generally be divided into two types: multilayer structures and inorganic/organic composites. Multilayer structures are typically formed by gas phase deposition or from the self-assembly of monolayers. Inorganic/organic composites can be formed by sol-gel techniques, bridging between clusters, or by coating nanoparticles, in polymer layers, for example.

V. PROPERTIES OF NANOCOMPOSITES

Nano-composites have gained much interest recently. Significant efforts are underway to control the nano-structures via innovative synthetic approaches. The properties of nano-composite materials depend not only on the properties of their individual parents but also on their morphology and interfacial characteristics.

The physical, chemical and biological properties of nano materials differ from the properties of individual atoms and molecules or bulk matter. By creating nano particles, it is possible to control the fundamental properties of materials, such as their melting temperature, magnetic properties, charge capacity and even their colour without changing the materials' chemical compositions.

Nano-particles and nano-layers have very high surface-to-volume and aspect ratios and this makes them ideal for use in polymeric materials. Such structures combine the best properties of each component to possess enhanced mechanical & superconducting properties for advanced applications.

The properties of nano-composite materials depend not only on the properties of their individual parents but also on their morphology and interfacial characteristics. Some nanocomposite materials could be 1000 times tougher than the bulk component. The general class of nanocomposite organic/inorganic materials is a fast growing area of research.

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 (Mo3Se3-)n chains and clusters. Thus, nanocomposites promise new applications in many fields such as mechanically reinforced lightweight components, non-linear optics, battery cathodes, nano-wires, sensors and other systems.

Inorganic layered materials exist in many varieties. They possess well defined, ordered intralamellar space potentially accessible by foreign species. This ability enables them to act as matrices for polymers yielding hybrid nano-composites. Lamellar nanocomposites represent an extreme case of a composite in which interface interactions between the two phases are maximized. By engineering the polymer-host interactions, nanocomposites could be produced with the broad range of properties. Lamellar nano-composites can be divided into two distinct classes viz. intercalated and exfoliated. In the former, the polymer chains are alternately present with the inorganic layers in a fixed compositional ratio and have a well-defined number of polymer layers in the intralamellar space.

In exfoliated nano-composites, the number of polymer chains between the layers is almost continuously variable and the layers stand >100 Å apart. The intercalated nano-composites are useful for electronic and charge transport properties. On the other hand, exfoliated nano-composites possess superior mechanical properties. For example, the electronics industry utilizes materials that have high dielectric constants and that are also flexible, easy to process, and strong. Finding single component materials possessing all these properties is difficult.

The most commonly used ceramic materials with high dielectric constant are found to be brittle and are processed at high temperatures, while polymer materials, which are very easy to process have low dielectric constants. Composite materials having micron-scale ferroelectric ceramic particles as the filler in liquid crystal polymer, fluoropolymer, or thermoplastic polymer matrices do not possess ideal processing characteristics and are difficult to form into the thin uniform films used for many microelectronics applications. Here comes the necessity of utilizing nanocomposite materials having a wide range of materials mixed at the nanometer scale.

By optimized fabrication process and controlled nano-sized second phase dispersion, thermal stability and mechanical properties such as adhesion resistance, flexural strength, toughness & hardness can be enhanced which can result into improved nano-dispersion.

The possibilities of producing materials with tailored physical & electronic properties at low cost could result in interesting applications ranging from drug delivery to corrosion prevention to electronic/automotive parts to industrial equipment and several others.

Nanocomposites are materials that incorporate nanosized particles into a matrix of standard material. The result of the addition of nanoparticles is a drastic improvement in properties that can include mechanical strength, toughness and electrical or thermal conductivity. The effectiveness of the nanoparticles is such that the amount of material added is normally only between 0.5 and 5% by weight.

Typically, nanocomposites are clay, polymer or carbon, or a combination of these materials with nanoparticle building blocks. They have an extremely high surface to volume ratio which dramatically changes their properties when compared with their bulk sized equivalents. It also changes the way in which the nanoparticles bond with the bulk material. The result is that the composite can be many times improved with respect to the component parts. Some nanocomposite materials have been shown to be 1000 times tougher than the bulk component materials.

Nanocomposites can dramatically improve properties like:

- Mechanical properties including strength, modulus and dimensional stability
- Electrical conductivity
- Decreased gas, water and hydrocarbon permeability
- Flame retardancy
- Thermal stability
- Chemical resistance

VI. BENEFITS OF NANOCOMPOSITES

In general, nanocomposites exhibit gains in barrier, flame resistance, structural, and thermal properties yet without significant loss in impact or clarity. Because of the nanometer-sized dimensions of the individual platelets in one direction, exfoliated Nanomer nanoclays are transparent in most polymer systems. However, with surface dimensions extending to 1 micron, the tightly bound structure in a polymer matrix is impermeable to gases and liquids, and offers superior barrier properties over the neat polymer. Nanocomposites also demonstrate enhanced fire resistant properties and are finding increasing use in engineering plastics.

Recent efforts have focused upon polymer-layered silica nanocomposites and other polymer-clay composites. These materials have improved mechanical properties without the large loading required by traditional particulate fillers. Increased mechanical stability in polymer-clay nanocomposites also contributes to an increased heat deflection temperature. These composites have a large reduction gas and liquid permeability and solvent uptake. Traditional polymer composites often have a marked reduction in optical clarity; however, nanoparticles cause little scattering in the optical spectrum and very little UV scattering.

Although flame retardant additives to polymers typically reduce their mechanical properties, polymer-clay nanocomposites have enhanced barrier and mechanical properties and are less flammable. Compressioninjection molding, melt-intercalation, and co-extrusion of the polymer with ceramic nanopowders can form nanocomposites. Often no solvent or mechanical shear is needed to promote intercalation.

The Nanocomposites 2000 conference has revealed clearly the property advantages that nanomaterial additives can provide in comparison to both their conventional filler counterparts and base polymer. Properties which have been shown to undergo substantial improvements include:

- Mechanical properties e.g. strength, modulus and dimensional stability
- Decreased permeability to gases, water and hydrocarbons
- Thermal stability and heat distortion temperature
- Flame retardancy and reduced smoke emissions
- Chemical resistance
- Surface appearance
- Electrical conductivity
- Optical clarity in comparison to conventionally filled polymers

Other benefits from nanocomposites include improvement in modulus, flexural strength, heat distortion temperature, barrier properties, and other benefits and, unlike typical mineral reinforced systems, they are without the conventional trade-offs in impact and clarity.

In plastics the advantages of nanocomposites over conventional ones don't stop at strength. The high heat resistance and low flammability of some nanocomposites also make them good choices to use as insulators and wire coverings. Another important property of nanocomposites is that they are less porous than regular plastics, making them ideal to use in the packaging of foods and drinks, vacuum packs, and to protect medical instruments, film, and other products from outside contamination.

Particle Loadings

In addition it is important to recognize that nanoparticulate/fibrous loading confers significant property improvements with very low loading levels, traditional microparticle additives requiring much higher loading levels to achieve similar performance. This in turn can result in significant weight reductions (of obvious importance for various military and aerospace applications) for similar performance, greater strength for similar structural dimensions and, for barrier applications, increased barrier performance for similar material thickness.

VII. THE FUTURE OF NANOCOMPOSITES

The number of commercial applications of nanocomposites have 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 key areas in the next five to ten years:

- Drug delivery systems
- Anti-corrosion barrier coatings
- UV protection gels
- Lubricants and scratch free paints
- New fire retardant materials
- New scratch/abrasion resistant materials
- Superior strength fibres and films

Improvements in mechanical property have resulted in major interest in nanocomposite 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.
More general applications currently being considered include usage as impellers and blades for vacuum cleaners, power tool housings, mower hoods and covers for portable electronic equipment such as mobile phones, pagers etc.

According to Cutting Edge (2001), today, nanocomposite research is widespread and is conducted by companies and universities across the globe. They listed the plastic suppliers who have already commercialized nanocomposite materials to include Basell USA, Bayer, Dow Chemical, Eastman Chemical, Mitsubishi Gas Chemical, Nanocor, Triton Systems, Honeywell, and RTP Co. however, most of these efforts are currently focused on either polyolefins or nylons, but, in theory, the clay nanoparticles could be used in any resin family.

Leaversuch (2001), explained that "optimism surrounding these novel materials has increased since they burst into industry consciousness two or three years ago, and exploratory effort has intensified as a growing body of data substantiates the potential established by nylon/clay nanocomposites, emerging polyolefin versions, and a range of other resin matrixes and nano-fillers….the promise of nanocomposites is undiminished."

From all indications it shows that the momentum is building. The success of Honeywell, Mitsubishi Gas and Chemical, Bayer, Triton Systems and Nanocor will lead to other successes. As production reaches a sufficient scale, incorporating the clay into polymers will become more cost-effective as well. Equipment recalibration used for conventional plastic resins will also show success.

The popularity of nanocomposites comes from the fact that a little goes a long way. It 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. It has very high impact in developing a new generation of composites with enhanced functionality and a wide range of applications. The data on processing, characterization and applications helps researchers in understanding and utilizing the special chemical and material principles underlying these cutting-edge polymer nanocomposites.

Although Nanocomposites are realizing many key applications in numerous industrial fields, a number of key technical and economic barriers exist to widespread commercialization. These include impact performance, the complex formulation relationships and routes to achieving and measuring nanofiller dispersion and exfoliation in the polymer matrix. Investment in state-of-the-art equipment and the enlargement of core research team's is another bottleneck to bring out innovative technologies on nanocomposites. Future trends include the extension of this nanotechnology to additional types of polymer system, where the development of new compatibility strategies would likely be a prerequisite.

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