

Polymer Composites Containing Functionalized Nanoparticles and the Environment

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14.1 Introduction

Nanoparticles in general and functional nanoparticles in particular are of considerable interest for various industrial and technological applications due to their small dimensions, enhanced functional properties and features they offer that are not available in particles with larger dimensions or bulk of same materials [1-3]. The European Commission (EC) defines a nanomaterial as [4]: "A natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50 % or more of the particles in the number size distribution, one or more external dimensions is in the size range 1-100 nm." Nanoparticles can be manufactured from various materials including metals, ceramics/glass, polymers, and semiconductors [5-11]. These particles can be produced in various shapes such as sphere [12], cube [13], rod [14], nanoplate [15], and others [16]. The properties of nanoparticles are closely linked to their size, shape, and surface functionalities. These variations and tailorable properties have led to a wide range of applications of this class of materials in the development of state-of-the-art materials to be used in structural applications, electronics, biomedicine, cosmetics, energy, catalysts, filters, and sensors [17]. As a result of their unique properties and a wide range of applications, the production of various nanoparticles has dramatically increased in recent years, which brings about the dilemma of their positive and negative effect on the environment and human health. These materials can be used in biological applications, water treatment, biosensors, filters, and energy technologies to save the environment and provide higher life quality for humankind. However, even nanoparticles synthesized from biologically inert materials can be harmful to

the cell by damaging cell membrane, disrupting cell function, or altering the genetics of the cell by attaching to its DNA [18].

Nanoparticle toxicology is a science of studying the ability of nanoparticles to damage or change the function of cells, genes, and living organs and determine the mechanism of that damage [19]. However, nanotechnology boundaries are always being pushed to create extremely small size particles with dimensions smaller than that of cellular structures [20,21]. The extremely small size of particles induces a significant

impact on nanoparticles' properties and behavior in the biological environment due to their ultrahigh surface area and shape factors such as extreme sharp edges, which have led to the intrinsic toxicity of such materials [22-24]. The nanoscale dimension renders the chemical/physical properties of the particles in a way that toxicological behavior of nanoparticles cannot be extrapolated from information and available data of larger particles of the same composition [24,25].

One may say that in polymeric nanocomposites, nanoparticles are fundamentally bound up in the structure of polymeric nanocomposites, but there is the potential for exposure to nanoparticles and nanomaterials throughout the product chain during manufacture, application, and waste management [22]. One issue making particle toxicology more complex than other toxicology branches is the variation in behavior of nanoparticles of interest by several structural and environmental factors that enable the unfavorable effect of nanoparticles in diverse scenarios [22].

This chapter initially discusses the recent progress in the understanding of the toxic behavior of various nanoparticles that are used commercially and intensively in nanocomposite production. This section reviews these nanoparticles' effect on living organs by elaboration on mechanisms and parameters contributing to such behavior. In the second part of this chapter, different applications of nanocomposites to promote human quality of life and contributing to the wellbeing of the environment are discussed in selected areas to emphasize the importance of nanocomposites in technological advancements.

14.2 Toxicological and Exposure

The nanoparticles with dimensions in the range below 100 nm are prone to have a range of unexpected effects on biological systems. These particles are so small that they can pass through the phagocytic defense system without being detected, giving them access to blood flow and the nervous system, and they can also accumulate in the vital organs. Furthermore, these nanoparticles have the ability to interact with proteins and inactivate their function or create an autoimmune effect in living organs. Humans are exposed to nanoparticles by lung exposure through environmental air pollution, skin exposure through cosmetic products, and inhalation and consequent redistribution to other organs [21,26]. There are many knowledge gaps in our understanding on the toxicity of nanoparticles and their relations with particle size, roughness, shape, charge, composition, surface coating, and physiological mechanisms [24]. Therefore, a comprehensive understanding of the potentially harmful effects of nanoparticles is necessary to provide a safe facilitation of these materials to our

lives and ensure future wellbeing. In this section, a summary of nanotoxicological studies of some important nanoparticles with high volume use such as carbon nanotubes (CNTs), graphene, nanoclays, and various metallic nanoparticles is discussed and their toxicity mechanisms as well as the effect of nanoparticles' physical and chemical structure in the environment are deliberated when available.

14.2.1 Carbon Nanotubes

CNTs are the thinnest tubes humans have ever made. They are chemically and thermally very stable with diverse properties and broad application range [27-29]. Some of CNTs' distinguished properties are high strength, high toughness, extremely high surface area, and excellent thermal and electric conductivity. CNTs' diameter ranges from ~0.4 to 3 nm for single wall and from ~1.4 to 100 nm for multiwall nanotubes [30-32]. CNTs are long thin structures that can have length up to many several tens of micrometers. Fig. 14-1 exhibits the molecular representations of single-walled CNTs and multiwalled CNTs (MWCNTs) and their typical transmission electron micrographs.

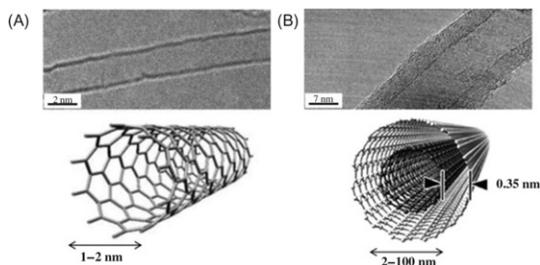


Figure 14-1 TEM images and schematic illustrations of CNT types showing typical diameters and separation between the graphene layers in MWCNT: (A) single-walled carbon nanotube (SWCNT) and (B) MWCNT.

CNTs are usually synthesized by one of the following techniques: Carbon-arc discharge, laser ablation of carbon, or chemical vapor deposition (CVD) [34]. The first two methods employ solid-state carbon precursors as carbon sources by vaporization at high temperature. On the other hand, CVD method utilizes hydrocarbon gases as carbon sources and metal particles as “seeds” for nanotube growth [35]. These CNT production methods require a high amount of energy and generate large amounts of byproducts, which limits their production in large scale and raises several environmental concerns. CNTs are one of the least biodegradable manmade materials. The insolubility in solvents and lipophilic behavior of CNTs make their removal from environment and organs almost impossible [36,37]. These CNTs can enter the environment at all stages of synthesis, processing, application, and disposal,

and exhibit their toxic properties. The toxicity and polluting effect of CNTs differ depending on their structural properties such as length, surface chemistry, and oxidative potential as well as the types of cells they are interacting with [38].

The health risk and environmental effect of CNTs strongly depend on their physical properties, shape, and surface functional groups. The toxicity of CNTs is a result of both their physical and chemical properties. The intensive interactions between CNTs and cell membranes may cause physical damage and consequent cell death. Moreover, CNTs are able to chemically interact with cells and promote cellular oxidative stress, which can lead to cell malfunction or even cell death [39]. Size is one of the most important parameters determining the toxicity of CNTs, for example, CNTs longer than 20 μm cause the same types of pathology that long biopersistent fibers cause such as fibrosis, cancer, pleural changes, and mesothelioma. On the other hand, CNTs with shorter length of 15–20 μm act like nanoparticles in which adverse effect and toxic behavior are driven by the small size and large surface area of the CNTs [26]. The surface functionalities of CNTs play a critical role in their behavior, toxicity, and state of aggregation in the environment. The surface functionalization of CNTs through acid treatments or any other methods can change their dispersion behavior significantly [40]. The surface functionalized CNTs displayed high mobility in water, which assesses the potential migration in natural porous media [41]. In addition, the high surface area and consequent high surface energy of CNTs lead to attachment of other potential pollutants and their transport throughout the environment [42]. Furthermore, the surface functional groups determine CNTs' interaction with cells and consequent toxic effects. The surface charge of CNTs is another parameter influenced by surface functionalization, which plays a critical role in the toxicity of CNTs. Shen et al. [43] showed that in vitro cytotoxicity and the biocompatibility of functionalized CNTs is largely dependent on their surface potential. They applied polyethyleneimine functionalization on the acid-treated CNT, which resulted in water-soluble and stable CNTs. The mentioned study showed that neutral and negatively charged CNTs are nontoxic to targeted cells at a concentration up to 100 $\mu\text{g}/\text{mL}$, whereas positively charged MWCNTs showed toxicity at 10 $\mu\text{g}/\text{mL}$ [43]. Nevertheless, Pulskamp et al. [44] did not observe acute toxicity for three commercial grades of nonfunctionalized single-walled CNTs, whereas Jos et al. [45] confirmed the cytotoxicity of carboxylic functionalized single-walled CNTs on differentiated and nondifferentiated Caco-2 cells derived from a human intestinal adenocarcinoma at concentrations higher than 100 $\mu\text{g}/\text{mL}$. In another work, Saxena et al. [46] observed that acid functionalized single-walled CNT exerted stronger toxic effects in vitro (cytotoxicity, cell cycling inhibition, and apoptosis) and in vivo in comparison with unmodified single-walled CNT, and they showed that those toxic effects could be reversed by neutralizing the negative surface charges. Magrez et al. [29] showed that the toxicity of CNTs increase significantly when carbonyl (C=O), carboxyl (COOH), and/or hydroxyl (OH) groups are present on their surface without any clarification on the exact mechanisms. In contrast, Sayes et al. [47] observed that an increase in the degree of sidewall functionalization of single-walled CNTs decreases their cytotoxic property.

In general, size, shape, and surface charge of nanoparticles are believed to be the three most important factors affecting the nanoparticles' toxicity. However, the toxic behavior of

CNTs is also related to environmental parameters such as pH, temperature, and light. In fact, the toxicity of nanoparticles in general and CNTs, in particular, is a complicated process related to the whole effect of their physical properties interacted with specific biomolecules or the releasing contents of dissolved toxic ions in biological media. Therefore, due to the contribution of numerous effective parameters in CNT polluting and toxicity, the investigation, control, and prediction of its behavior and effects on organs and environments is a challenging task. However, a high level of fundamental understanding of biocompatibility and effects of CNTs on human health and environment should be achieved to ensure the safe integration of CNT-based products in our lives. Considering this information, extra precautions in manipulation and functionalization of CNTs are needed to be taken in manufacturing and applications of

functionalized CNTs where CNTs are in direct contact with living organisms.

14.2.2 Graphene

Graphene with its unique 2D structure and exceptional physical and chemical properties has attracted the attention of scientists and engineers in various advanced applications such as development of novel polymeric composites with unique properties [15,48-50]. Graphene is one of the strongest materials, having a theoretical Young's modulus of 1060 GPa and an ultimate strength of 130 GPa, and also high specific surface area, which makes it a suitable candidate for nanocomposite production with extended physical and chemical properties [48]. These novel nanocomposite materials have great potential for various applications, ranging from high-performance structures, energy storage devices, electrically conductive polymeric materials, as well as antibacterial materials [51].

Several graphene grades can be found in the graphene family materials such as few-layer graphene, graphene nanosheets, graphene oxide (GO), and reduced graphene oxide (rGO) and graphite as shown in Fig. 14-2 [52]. Each member of the graphene family has unique behavior and sometimes diverse properties compared with others. Graphene family products are growing at a rapid rate and they are commercialized in various applications [53]. This increases the graphene production rate and consequently their release to the environment. The graphene/polymer nanocomposites may release graphene during manufacturing, degradation of the polymeric matrix, or direct environmental applications such as water or soil treatment [54-56]. The released graphene into the environment has the high potential to have significant adverse impacts at different levels from bacteria and mammalian cells to animals.

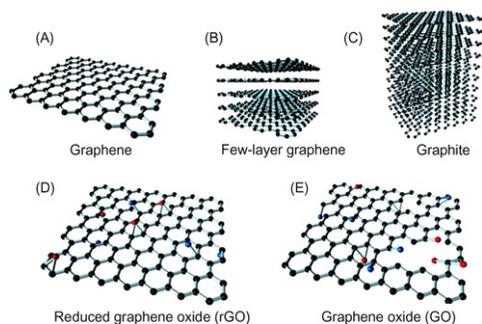


Figure 14-2 Graphene family nanomaterials. (a) Graphene, (b) few-layer graphene, (c) graphite, (d) reduced graphene oxide (rGO), and (e) graphene oxide (GO)

Reprinted from Kiew SF, Kiew LV, Lee HB, Imae T, Chung LY. Assessing biocompatibility of graphene oxide-based nanocarriers: a review. *J Control Release* 2016;226:217-28, by permission of Elsevier.

Herein, we will try to briefly review the available literature to provide an understanding on the effect of graphene-based materials on various organisms, the mechanisms involved in their toxicity, and also compare their toxicity with other similar materials. It is well known that GO and rGO as two renowned members of the graphene family show higher antibacterial activity over graphite oxide and graphite. This stems from their finer size and thinner layers, which give them the sharp edges to damage the plasma membranes on bacterial cells and kill the cell [39,57]. The sharp edges of GO and rGO are not available in other carbon

nanomaterials such as carbon black, which restricts their antimicrobial activities through the mentioned mechanism. In addition, GO shows higher cytotoxicity compared with rGO; this is because of its higher dispersibility in aqueous media, and presence of active surface functional groups, which promote the possibility of direct contact with cells and inducing higher intracellular oxidative stress [49]. Contrarily, some studies showed higher toxicity of rGO is correlated with its thinner structure in the absence of oxygen functional groups (0.34 nm) compared with that of GO (1 nm), which creates sharper edges to damage the cell membrane easily [58,59]. Furthermore, it is observed that higher electrical connectivity of rGO increases the oxidative stress on intracellular glutathione by enhancing the electron transfer between the edges to membranes which promotes enhancing its toxic effect on cells [60-62]. On the other hand, the hydrophobicity of rGO upholds its interaction with the cells' outer wall, which can hinder the nutrient absorption and gas exchange across the cell membrane [63,64].

The environment and cell type have a disputable effect on the toxicity of graphene. A small change in the environments may change the graphene's structure, transport, aggregation, and toxicity [65]. GO can go through a reduction process under light exposure or through exposure to chemical compounds [66-68]. Furthermore, biodegradability is another issue that should be addressed while discussing the concerns around the environmental effects of

graphene and its derivatives. GO has shown biodegradability potential in presence of enzymes such as myeloperoxidase [69]. Surface functionalization is another parameter that influences the toxicity of graphene family materials and alters their biodegradability and dispersibility on the environment [70]. GO has the ability to be degraded by low concentrations of enzymes while rGO shows resistance to enzyme degradation [71]. The point is oxidation of graphite creates defect sites on the structure promoting the biodegradation of graphene. However, excessive functionalization with larger functional groups may prevent their biodegradation [72,73]. Nevertheless, the number of effective enzymes to be used in

biodegradation of nanomaterial is very restricted and more biodegradation studies are needed to characterize better and more effective enzymes to provide biodegradability of graphene and minimize its effect on the ecosystem [70].

14.2.3 Nanoclays

The first polymer nanocomposite was a polymer-clay hybrid that was invented at Toyota Central R&D Labs, Inc. (Toyota) [74]. In the mentioned hybrid polymer composite system a small amount of silicate layer of clay mineral is randomly and homogeneously dispersed on a molecular level in a polymer matrix [75]. Nanoclays are layered mineral silicates, which are one of the common additives for polymer nanocomposite production with increased strength, modulus, and toughness and improved barrier and flame-retardant properties [76,77]. Clay-based polymeric nanocomposites possess a large portion of the nanocomposite market in various application areas.

Clays are abundant, highly stable, inexpensive, and believed to be an environmentally friendly nanoadditive [73]. Montmorillonite is a natural clay and the most frequently used nanoclay in the preparation of polymer nanocomposites with plate-like particles called platelets [78]. Montmorillonite platelets have an average thickness of only 1 nm, while their dimensions in length and width can be measured up to 1 μm [78]. Fig. 14-3 shows the structure of montmorillonite clay, which consists of two tetrahedral sheets covered with one octahedral sheet in between [79]. Despite the several useful biological and environmental applications of nanoclays, their nanoscale size enables them to penetrate to the cell membranes, and interfere with cellular processes [78,80]. Several mechanisms contribute to toxicity of nanoclays including decrease in both cellular growing rate, morphological changes of cell, cellular proliferation, mitochondrial damage, reactive oxygen species generation, and

DNA alteration [81-84]. It worth noting that the prudency of each damage type is closely related to studied cell, dosage, and surface functionalization of clays.

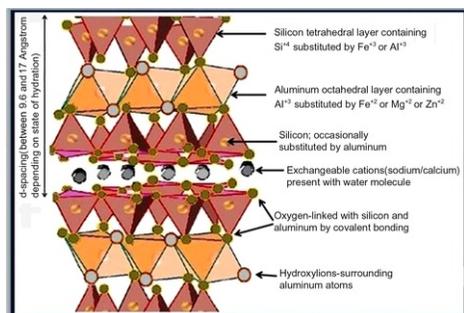


Figure 14-3 Structural unit of montmorillonite nanoclay.

Reprinted from [Kaseem M, Hamad K, Ko YG. Fabrication and materials properties of polystyrene/carbon nanotube \(PS/CNT\) composites: a review. Eur Polym J 2016;79:36-62](#); [Jayrajsinh S, Shankar G, Agrawal YK, Bakre L. Montmorillonite nanoclay as a multifaceted drug-delivery carrier: a review. J Drug Deliv Sci Technol 2017;39\(Suppl. C\):200-9](#), by permission of Elsevier.

In the clay structure, the interlayer space (known as the clay gallery) contains exchangeable cations such as Na⁺ or K⁺ [85]. Organomodification of nanoclays is a method to replace these cations with organic cationic surfactants. This organomodification increases gallery spacing, improves the compatibility, makes clay hydrophobic, and enhances its compatibility with most of the polymeric matrices [86]. The organomodification or functionalization of clays with organic chains plays a critical role in their cytotoxic response. Some studies find that organomodified clays have greater toxicity compared with unmodified ones [78,87] whereas other findings express lower toxicity of modified clays compared with their unmodified counterparts [88,89]. These studies also express the importance of functional group type used for organomodification on the toxicity of nanoclays [90-92].

The clay's physical structure and geometry (platelet or tubular) have significant effect on its toxicity [93]. Verma et al. [81] detected a noticeable difference in the number of detached and deformed cells exposed to platelet-type nanoclays compared with cells in contact with tubular clays, which indicates that platelet structured nanoclays are more cytotoxic than tubular type. Their study showed that tubular clays, known as halloysite nanotubes, do not show any toxic effect until doses of 250 µg/mL, while platelet nanoclays cause toxicity at 25 µg/mL [81].

Given the complex and uncertain effects of nanoclays on biological environments, systemic management, analysis, and precautions are required to assess and minimize the exposures during their manipulation, handling, and disposal. In addition, more research efforts are necessary to evaluate and understand the mechanisms of toxicity of nanoclays in cells and find a proper solution to design safe products of nanoclay-based polymeric nanocomposites for future applications.

14.2.4 Metal Nanoparticles

The incorporation of metal nanoparticles into polymeric matrices is an emerging area to further extend the applications of polymeric nanocomposites. The quantum size effects on metal nanoparticles give them great promise in many technical and also medical applications [94]. These unique properties can be tailored by controlling these metal nanoparticles' size, shape, and preparation methods. Metal nanoparticle-based polymeric nanocomposites provide enhanced performance and multifunctionalities as well as promising potential applications in electronics, optics, environmental, and biotechnological applications, which may not be possible with larger metal particles. Metal nanoparticles can be categorized into metals, metal oxides, and other metal-containing nanoparticles [95,96]. The wide range of application of metallic nanoparticles and high volume production connect this class of materials with some environmental effects uncertainties and serious risks. These materials can enter living organisms including the human body through active or passive pathways and have the high potential to create unrecoverable damage because of their activated toxicity due to their intrinsic properties and also their nanoscale size [97]. In this part, the

environmental effects of selected metal nanoparticles, which are used intensively in polymer nanocomposite productions such as titanium dioxide (TiO₂), zinc oxide (ZnO), and silver (Ag) nanoparticles, are discussed in detail including the effective parameters and corresponding mechanisms in their toxicity.

TiO₂ is a naturally occurring mineral that can be categorized into anatase, rutile, or brookite types based on its crystal structure [98]. TiO₂ nanoparticles have one of the highest production rates worldwide among other nanoparticles [99]. TiO₂ is an effective reinforcing agent for several polymeric matrices and it also provides polymeric materials with several unique properties. TiO₂ nanoparticle is a large band gap semiconductor, which gives it exceptional electronic, optical, thermal, and photocatalytic properties. These unique functionalities of TiO₂ nanoparticles are of interest for the development of several functional polymeric nanocomposites [100-102]. TiO₂ nanoparticles show both beneficial and toxic effects on nature depending on their intrinsic properties and also the environmental factors [103]. TiO₂ have been accepted as safe materials and their cytotoxicity is often neglected whereas there are reports on their toxicity through generation of reactive oxygen species, increased cell adhesion, and alteration on carbohydrate metabolism [104-106]. Furthermore, TiO₂ nanoparticles have genotoxicity properties and they can interact with DNA of cells [107]. However, there are several conflicting results on toxicities of TiO₂ nanoparticles, some claiming no toxicity effect and some high toxic effect of these particles in the living organs. These conflicts stem from various morphology, crystal structure, size, purity levels surface areas, and also conducted test conditions [108]. To resolve these conflicts, a clear understanding of the molecular mechanisms behind the toxic and nontoxic responses of TiO₂ nanoparticles is needed [104].

The crystal structure of TiO₂ nanoparticles plays a critical rule in their toxic behavior [109]. In nature, TiO₂ has three common crystalline polymorphs, namely brookite, anatase, and rutile as shown in Fig. 14-4 [110]. However, only rutile and anatase TiO₂ are generally manufactured in titanium dioxide commercial applications. The relative toxicity of each

crystal structure of TiO₂ nanoparticles with respect to biological systems is broadly debated; no solid conclusion is available. In general, it is accepted that anatase TiO₂ nanoparticles are more active under light exposure or dark environment and generate higher reactive oxygen species and consequent DNA damages compared with other counterparts with different crystal structures [111,112]. The anatase TiO₂ nanoparticles are able to spontaneously generate reactive oxygen species whereas rutile TiO₂ nanoparticles do not exhibit similar behavior [112]. It is worth noting that anatase nanoparticles have a high affinity to proteins, mainly impairing mitochondrial function whereas the rutile TiO₂ nanoparticles have higher affinity to phospholipids, mainly targeting the plasma membrane and the lysosome membrane, and causing reactive oxygen species-independent cell death [109]. Furthermore, the rutile TiO₂ nanoparticles are able to induce hydrogen peroxide and oxidative DNA damage in the absence of light while anatase TiO₂ nanoparticles do not have this effect [113]. Additionally, some studies showed the higher toxicity of a mixture of anatase and rutile particles and its higher abilities to create DNA damage in the absence of light compared with individual anatase or rutile TiO₂ due to contribution of multiple toxicity mechanisms [113].

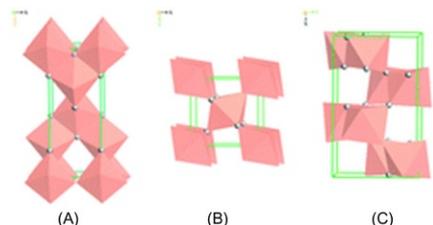


Figure 14-4 Representation of three TiO₂ polymorphs: (A) anatase, (B) rutile, and (C) brookite forms.

Reprinted from Liao Y, Que W, Jia Q, He Y, Zhang J, Zhong P. Controllable synthesis of brookite/anatase/rutile TiO₂ nanocomposites and single-crystalline rutile nanorods array. *J Mater Chem* 2012;22(16):7937-44, by permission of Royal Society of Chemistry.

TiO₂ nanoparticles can be distributed to all organs or tissues from the original site upon entering the blood and deposited in the liver, lung, kidney, and other organs, which can cause severe damage to and malfunction of that organ [99,114,115]. Nanoparticles in general and TiO₂ nanoparticles, in particular, can enter the human/animal body through various routes such as oral, dermal, or injection and cause various toxicities in different organs [99]. Studies show that oral exposure to TiO₂ nanoparticles induces hepatic histopathologic damage, with alterations in serum lactate dehydrogenase and alpha-hydroxybutyrate dehydrogenase levels indicating myocardial damage as well as neurotoxicity and brain damage [116,117]. The high amount of application for TiO₂ nanoparticles in cosmetic products makes dermal exposure an important issue. However, there are conflicting findings in the literature in which some groups claimed that TiO₂ nanoparticles are unable to penetrate human skin whereas others present opposite findings [118-122]. Despite several recent studies on the toxicity of TiO₂, its toxicity mechanisms and its effect on the ecosystem are not completely understood. Therefore, further investigations and detailed research activities are required to understand the potential health effects and plan proper risk assessment procedures to pave the way for this useful material implementation in future applications.

Zinc oxide (ZnO) nanoparticle is another metallic nanoparticle widely used in the polymeric nanocomposite manufacturing. ZnO is an n-type semiconductor with wide band gap energy of 3.3 eV making it a suitable choice for a broad range of applications. The incorporation of ZnO nanoparticle into polymeric matrices provides them with various functionalities including enhanced mechanical performance, permeability, flame resistance, UV-shielding, antimicrobial activities, and unique thermal and electrical properties [73,123-127]. Even though ZnO is listed as a Generally Recognized as Safe material by the US Food and Drug Administration (21CFR182.8991) and it is widely used in products that have direct contact with humans such food packaging and coatings applications, there is a myriad of research reporting the toxic behavior of ZnO nanoparticles [128-131]. The ZnO nanoparticles have the ability to induce morphological modifications, oxidative stress, lipid

peroxidation, cytotoxicity, genotoxicity, and chromosomal breakage forms of toxicities [132-137]. The toxicity of ZnO nanoparticles can be influenced by ZnO nanoparticle surface composition, size, and shape [133,138,139]. It is an accepted fact that antibacterial activity of ZnO nanoparticle increases with a reduction in particle size [139]. In addition, the shape of ZnO nanoparticles plays an important role in their toxic behavior [140]. At a fixed ZnO nanoparticle size and surface area, nanorod ZnO nanoparticles are more toxic than the corresponding spherical ones [140]. In addition to the toxicity mechanism correlated with the nanoscale size of the ZnO nanoparticles, it is shown

that release of zinc ions is another toxicity mechanism in which these ions show **induced** higher toxicity compared with ZnO nanoparticles themselves [141].

The surface functionalization is another important parameter influencing the toxicity of ZnO nanoparticles. In addition, the correlation between surface functionality and toxicity of ZnO nanoparticles can be an effective way to modify the toxicity of ZnO nanoparticles to have specific cellular interactions with the biological molecules and preserve their functional properties, which will open up several novel applications for this group of nanomaterials [142-146]. In this regard, Ramasamy et al. [147] fabricated SiO₂-coated ZnO nanoparticles in which coated ZnO nanoparticles exhibit less cytotoxicity compared with uncoated ZnO nanoparticles. The mentioned work correlates that the decreases in cytotoxicity with fewer surface interactions of ZnO nanoparticles with cells after coating by SiO₂, decreased in the release rate of zinc ion, and changes on the hydrophilicity of the surface after coating of ZnO nanoparticles [147]. In another study, Hsiao et al. [148] reduced the cytotoxicity of ZnO nanoparticles by coating them with a TiO₂ layer applying a sol-gel method and they observed moderate toxicity on the ZnO/TiO₂ core/shell structure compared with uncoated ZnO nanoparticles. The TiO₂ coating reduces toxicity by decreasing the release of zinc ions, also restricting the contact area of the ZnO cores with the cell. Luo et al. [149] applied polyethylene glycol coating on ZnO nanoparticles and reduced the cytotoxicity of ZnO nanoparticles. These findings bespeak the important role of the surface properties of ZnO nanoparticles on their cytotoxicity. Despite these studies, the toxicity mechanism of ZnO particles is still not well understood and further investigations are required to understand the mechanisms involved in the toxicity of ZnO nanoparticles and develop the safety rules regarding exposure to ZnO nanoparticles.

Silver (Ag) nanoparticles with extraordinary optical, electronic, catalytic, and more importantly antibacterial properties have found great applications in the development of functional polymer nanocomposites [150-152]. The widespread use of Ag nanoparticles in toys, clothing, and food packaging products raises serious concerns about their effects on human health and ecosystems. These concerns bespeak the necessity of detailed safety evaluations and obtaining a clear understanding of the impact of Ag nanoparticles on human health and the environment [152,153]. Ag nanoparticles are one of the most effective and frequently used antimicrobial agents in polymeric products [154,155]. The broad range of Ag nanoparticles' applications increases the possibility of exposure and consequent severe damage risks to the ecosystem. Despite several proposed mechanisms for the toxicity of Ag nanoparticle, its exact mechanisms are not well understood yet [156]. Some of the proposed mechanisms

are physical damage and penetration that cause cell malfunction [157], dissolution of Ag⁺ from the Ag [158], and stimulation of reactive oxygen species [159]. Various factors that can influence the level of toxicity and its mechanism are particle size, surface properties, and shape [160,161]. Nevertheless, as silver in its metallic state is considered as an inert metal, it can easily react with moisture and get ionized, and is highly reactive and able to bind to proteins, DNA, and RNA [162].

It is suggested that Ag nanoparticle morphological properties indirectly affect antimicrobial activity and toxicity by influencing the Ag⁺ release rate [163]. Helmlinger et al. [160] correlated the dissolution kinetics with the particle size in which particles with a higher specific surface area (finer particles) show more toxicity than particles with smaller specific surface areas (larger particles). Considering the Ag⁺ release as the main toxicity source for Ag nanoparticles antibacterial and toxic activity, these activities can be manipulated by controlling the Ag⁺ release through tailoring the particle size, shape, applied coating, and the environmental parameters [163]. However, there are studies suggesting morphological factors of Ag nanoparticles as responsible for its toxic behavior rather than its ionized state. The nanoscale size of Ag nanoparticles is able to produce reactive oxygen species and oxidative stress, which can damage the cell [164-166]. On the other hand, some research proposes a combined effect in which Ag nanoparticles enter the cells and act as a source of Ag⁺, leading to cytotoxic and genotoxic damage known as the "Trojan horse" effect [73,167]. The high production in the increasing utilization of Ag nanoparticles in commercial products raises serious concerns about its environmental effects and their impact on the ecosystem in recent years. Therefore, more research and investigations are needed to enhance current understanding of their toxic behavior and address these issues for their further development.

14.3 Environmental Benefits and Application of Polymeric Nanocomposites

Despite several studies mentioning the adverse effect of nanoparticles and nanocomposites on the environment and the ecosystem, this class of materials brings about several novel and unique beneficial applications to serve nature and the ecosystem. In this section, some of the well-established environmental applications of polymeric nanocomposites that ease and protect human life, save the environment, and provide better future ecosystems are discussed. Packaging, membranes, and energy are the selected application areas, among others that nanotechnologies and especially polymeric nanocomposites have revolutionized.

14.3.1 Food Packaging by Nanotechnology and Nanocomposites

Advances in the food packaging industries as an essential part of today's economy have enabled effective transportation, distribution, and preservation of food and ensure its proper physical and physicochemical conditions at the delivery point. The desired packaging material should possess mechanical, optical, and thermal properties that prevent the transfer of unwanted substances such as microbial contamination, moisture, and oxygen into/from the

package. Over the last few decades, the utilization of polymers for food packaging has increased greatly because of their superior properties such as functionality, light weight, ease of processing, variety, and low cost over other traditional materials (metals, ceramics, and paper). However, pristine polymer-based packaging does not satisfy industry needs for a packaging that provides the capability to keep the packaged materials for a longer time. To address the mentioned limitations, polymeric nanocomposites prepared by functionalized nanoparticles provide an opportunity to produce the next-generation food packaging. Polymer nanocomposite-based packaging material shows several unique and enhanced properties such as high barrier, antimicrobial activities, and the capability to act as a sensor for the detection of food-relevant gases, or other molecules. In addition, the possibility to implement low amounts of nanoparticles and achieve higher enhanced properties compared with microcomposites has led to a reduction in cost. One of the novel packaging technologies enabled by functionalized nanoparticles is active and intelligent packaging in which the package materials are designed to interact with the food or the food environment. These interactions can be releasing, absorbing, or modifying substances into or from the packaged food or the environment surrounding. Fig. 14-5 represents some of the nanocomposite-based active packaging technologies [168]. The developments in this type of packaging materials are mostly focused on low permeable and antimicrobial films [168-170].

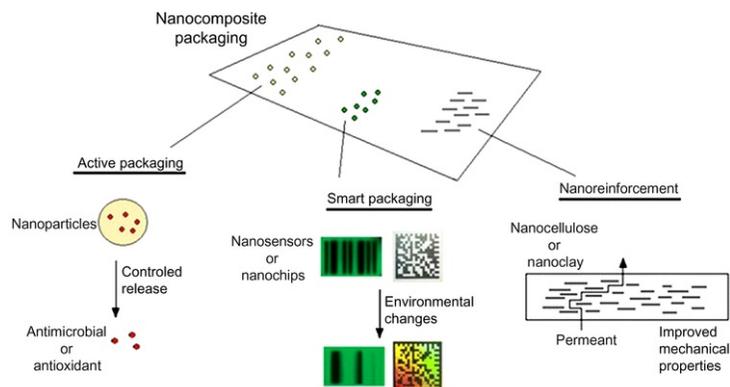


Figure 14-5 Applications of nanostructures in nanocomposite packaging. Active packaging can be developed through incorporation of nanoparticles encapsulating bioactive compounds with antimicrobial or antioxidant activity. The use of nanosensors or nanochips for development of smart/intelligent packaging may provide information about the condition of packaged food during transport and storage. Nanoreinforcement can be achieved by including nanofillers into biopolymer matrixes intended for packaging purposes, providing significant improvements in mechanical and barrier properties.

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As mentioned earlier, one of the main limitations restricting the widespread application of polymeric materials in food packaging is their relatively high permeability to small molecules and moisture, which has an adverse effect on the lifetime of the packaged product. One of the effective methods to enhance the barrier properties of the polymeric materials is blending them with specific nanoparticles. In nanocomposites, the gas barrier performance is determined by nanoparticle properties, matrix permeability, nanoparticle-matrix interactions, and the orientation of the nanoparticles. Clay and graphene are the most common nanoparticles used for enhancing the barrier properties of the polymeric composites because of their high surface area to thickness ratio, and impermeability to most of the gases and water vapor. Even relatively low additions of nanoclay to a polymer matrix stems a reduction of transport cross section, and also increase of transport paths of penetrant molecules and causes extreme reductions in permeability [171]. Moreover, the addition of nanoplatelets results in modification of polymer chain mobility and provides

lower available free volume to diffusing gas molecules and changes the solubility parameters [172,173]. The state of the dispersion and interface quality are also important parameters on nanocomposites' permeabilities, and play a critical role in the barrier performance of nanocomposites, which can be enhanced by proper surface modification of particles. However, low compatibility between polymer and nanoparticles results in a poor interfacial quality, which could lead to the presence of narrow gap around the nanofiller [174]. These gaps facilitate the flow and penetration of gas molecules and increase the permeability of the nanocomposite, which can have an adverse effect on the packaged material [174]. In addition, the polymer and nanoparticle compatibility state determines the dispersion state of the nanoparticles in the polymer matrix whose possible microstructures can be classified as phase-separated (microcomposite), intercalated, and exfoliated as shown in Fig. 14-6 [175]. In the case of phase-

separated nanocomposites, nanoplatelet tactoids are formed in the matrix and no separation of nanoplatelets occurs and polymer chains surround clay nanoplatelets without penetration between the layers. In intercalated nanocomposites, some of the molecular polymer penetrates between nanoplates while the overall order of the nanoplatelets is preserved. In the exfoliated nanocomposites, the layers are completely separated and dispersed individually within the continuous polymer matrix. The highest barrier improvements are expected from fully exfoliated polymer nanocomposites because in this state the nanoparticle platelets will have the highest surface area [176].

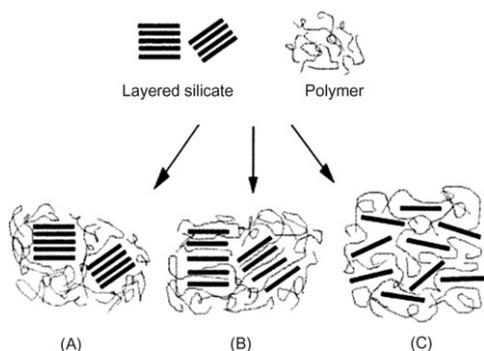


Figure 14-6 Scheme of different types of composite arising from the interaction of layered silicates and polymers: (A) phase-separated microcomposite, (B) intercalated nanocomposite, and (C) exfoliated nanocomposite.

Reprinted from Alexandre M, Dubois P. Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials. Mater Sci Eng Rep 2000;28(1):1-63, by permission of Elsevier.

Antibacterial activity is another desired property for food packaging materials that extends the shelf life and safety of food products by reducing the growth rate of microorganisms [177,178]. The polymeric nanocomposites based on metal nanoparticles such as Ag, TiO₂ and ZnO as antimicrobial agents showed high antimicrobial performance for a broad spectrum of microorganisms [179,180]. The presence of antibacterial nanoparticles in polymeric nanocomposite structure not only inhibits initial undesirable microorganisms but also averts the residual activity over time by controlled migration of the compound into the food [181]. The antibacterial activity of nanoparticles stems from various mechanisms including direct interaction with the microbial cells and causing damage in the cells' structure, oxidizing cell components, and producing reactive oxygen species or dissolved heavy metal ions [182,183]. Fig. 14-7 shows various mechanisms of antimicrobial activities exerted by nanomaterials [182].

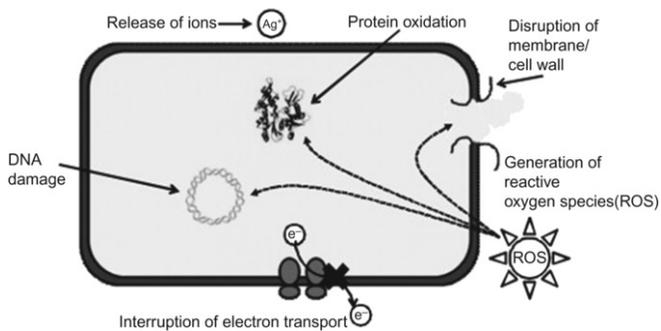


Figure 14-7 Various mechanisms of antimicrobial activities exerted by nanomaterials.

Reprinted from Li Q, Mahendra S, Lyon DY, Brunet L, Liga MV, Li D, et al. *Antimicrobial nanomaterials for water disinfection and microbial control: potential applications and implications. Water Res 2008;42(18):4591-602, by permission of Elsevier.*

14.3.2 Nanocomposites in Membrane Technology

Membrane technology is widely applied in various industries such as water treatment, molecular separations, biomolecule purification, environmental remediation, gas separation,

petroleum chemicals, and fuel production [184,185]. Polymeric membranes technology is an attractive alternative to inorganic membrane equivalents because of their high flexibility, low energy requirements, relatively low preparation cost, and environmental friendliness [186,187]. However, application of polymeric membranes is facing several challenges regarding their mechanical performance, thermal stability, permeability, and selectivity [188]. Nanomodifications and utilization of nanoparticles on the polymeric structures are considered as an effective way to address the mentioned challenges to produce membranes with higher reliability. These nanoparticle modified membranes are categorized into four distinct categories, namely, conventional nanocomposites, thin-film nanocomposites, thin-film composites with nanocomposite substrate, and surface located nanocomposites; these are schematically shown in Fig. 14-8 [186]. These nanocomposites can enhance the process efficiency and cost for various applications and have gained considerable attention in the cutting edge applications and high-performance membrane production in fuel cells, proton exchange membrane, sensors, batteries, solvents, and water treatment [189].

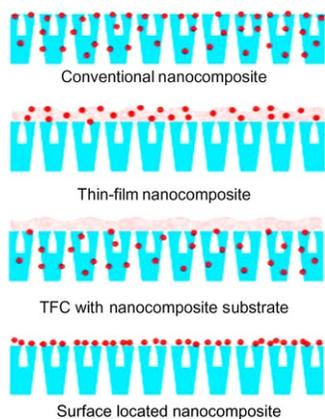


Figure 14-8 Typical types of nanocomposite membranes TFC, Thin-film composite.

Reprinted from Yin J, Deng B. *Polymer-matrix nanocomposite membranes for water treatment. J Memb Sci 2015;479:256-75, by permission of Elsevier.*

The nanocomposite structure combines the properties of each component and offers novel and unique properties that were not available previously. One of the important examples of nanocomposite technology development's effect on membrane application is the direct methanol fuel cell (DMFC). The conventional polymeric DMFC membranes' efficiency is constrained by the high rate of methanol permeation through a polymeric membrane, which causes the chemical reaction of the fuel with oxygen and depolarization of the cathode [190]. Therefore, it is highly desirable to have a membrane with reduced methanol

permeation. One of the examples of utilization of nanocomposites in this area of application is proposed by Song et al. [190] who used Nafion polymer-layered silicate nanocomposite as a membrane in which the strong interaction of Nafion polymer chains with exfoliated clays significantly decreased methanol crossover through nanocomposite membranes by only 1 wt.% organoclay fillers. In addition, nanoclay improved the thermal decomposition temperature and mechanical properties of the Nafion-based membrane [190].

Another example of the enhanced performance of membranes through the incorporation of nanoparticles is membranes used in water and wastewater treatment in which contamination of membrane reduces the flux by the time [187,191]. To address this issue, Bae et al. [192] fabricated TiO₂ entrapped membranes from three different polymers of polysulfone, polyvinylidene fluoride, and polyacrylonitrile to be used in filtration of the activated sludge. The TiO₂ entrapped membrane showed lower flux decline compared with neat polymeric membrane regardless of the polymeric matrix. In another work, Cao et al. [193] prepared a poly(ethylene oxide)/graphene oxide proton conductive membrane with enhanced performance compared with commercially available ones. The presence of GO in the poly(ethylene oxide) matrix increases the conductivity through the proton released from the COOH groups on the GO sheets as an ion conductivity mechanism. There are several other examples of nanocomposite-based membrane designs in the literature that can further improve the efficiency and generate a new generation of membranes for future applications in energy and various environmental applications, which can boost the future view of our ecosystem.

14.3.3 Nanocomposites in Energy Applications

Sustainable, efficient, and clean energy storage is another area that is taken to a whole new level by nanocomposite materials. Hydrogen is one of the renewable, convenient, safe, versatile, and clean energy fuel sources, which provides a significant reduction in the greenhouse gas emissions and fossil fuels consumption, and has high energy conversion efficiency [194,195]. The hydrogen storage systems are regarded as the key challenge in large-scale and commercial applications of hydrogen energy [196]. As pressurized tank and cryogenic liquid hydrogen techniques fail to satisfy the primary requirements for a hydrogen storage system such as being inexpensive, safe, delivering low efficiency, and material-based storage systems are expected to provide a final solution for this issue [196,197].

However, simple material systems with only one component failed to operate in ambient temperature ranges, and they suffer from low efficiency of fueling and serious concerns about their safety and slow kinetics [198]. The polymeric nanocomposites are considered to have potential promise for hydrogen storage among other counterparts [199]. Saner Okan et al. [27] combined the beneficial features of polypyrrole (PPy) with those of CNT and considerably improved the hydrogen storage capacity of the nanocomposite structure compared with the neat polymer and pure CNT. In the mentioned work, CNT and PPy adsorbed 0.46 wt.% and 0.14 wt.% hydrogen while their composite adsorbed 1.66 wt.% hydrogen [27]. Fig. 14-9A-C exhibit the nanostructures of PPy, CNT, PPy:CNT composite, respectively. Furthermore, Fig. 14-9D shows hydrogen sorption curves of pristine CNT, PPy, oxCNT, and

Py:CNT composite in the range of 0-9000 mbar pressure at room temperature indicating that pristine CNT, PPy, oxCNT, and Py:CNT adsorb 0.46, 0.14, 1.03, and 1.66 wt.% hydrogen, respectively bespeaking that the hydrogen storage properties of the produced nanocomposites are considerably higher than the individual components.

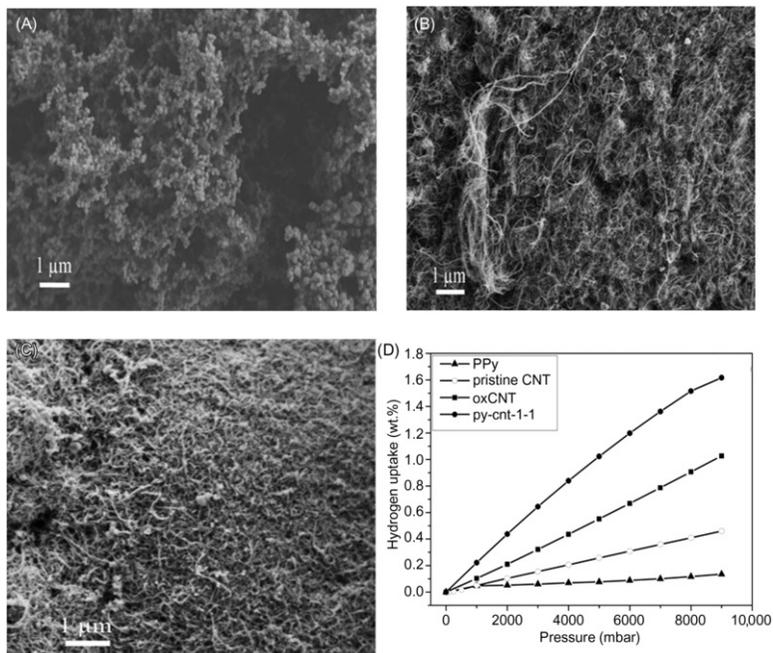


Figure 14-9 SEM images of (A) pristine PPy, (B) pristine CNT, (C) Py:CNT=1:1 composite, and (D) the comparison of adsorption isotherms of pristine CNT, PPy, oxCNT, and Py:CNT=1:1.

Reprinted from Okan BS, Zanjani JSM, Letofsky-Papst I, Cebeci FÇ, Menciloglu YZ. Morphology-controllable synthesis and characterization of carbon nanotube/polypyrrole composites and their hydrogen storage capacities. *Mater Chem Phys* 2015;167(Suppl. C):171-80, by permission of Elsevier.

In another study Muthu et al. [200] employed sulfonated poly(ether-ether-ketone) (SPEEK) and hexagonal boron nitride (h-BN) nanoparticles, to obtain high-performance hydrogen storage material and they enhanced the hydrogen storage from 0.66 wt.% for neat SPEEK to 2.98 wt.% in SPEEK-BN nanocomposite. Kim et al. [201] reported hydrogen adsorption in the polyaniline-vanadium oxide nanocomposites of up to ~1.8 wt% at 77 K and ~0.16 wt% at 298 K whereas neither polyaniline (~0.2 wt% at 77 K) nor pristine vanadium

pentoxide powder (~0.2 wt% at 77 K) were able to adsorb similar amount of hydrogen. Makridis et al. [202] used Mg-nanoparticles produced by laser ablation technique as shown in Fig. 14-10 and observed that Mg-nanoparticles in a polymer matrix exhibit more rapid hydrogen uptake compared with Mg-pure types (<20 minutes at 250°C) with a high capacity of 6 wt.% with excellent reversibility under vacuum at 250°C, which is a relatively low temperature with regard to the necessary ~330°C for Mg-bulk materials. These studies bespeak the high potential of nanocomposites for hydrogen storage in the near future.

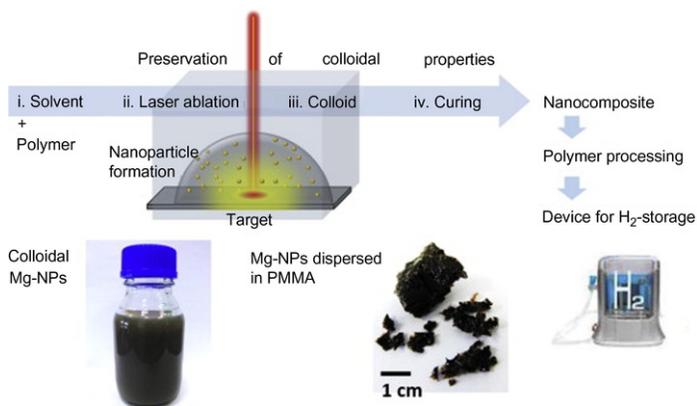


Figure 14-10 Laser-generated nanoparticles for nanocomposites.

Reprinted from Makridis SS, Gkanas EI, Panagakos G, Kikkinides ES, Stubos AK, Wagener P, et al. *Polymer-stable magnesium nanocomposites prepared by laser ablation for efficient hydrogen storage. Int J Hydrogen Energy* 2013;38(26):11530-5, by permission of Elsevier.

14.4 Conclusion and Outlook

The rapid development of nanoparticle-based nanocomposites has a huge impact on many technological areas. There are a vast variety of nanoparticles that are used in the preparation of polymeric nanocomposites in which a small change in their physical or chemical structure leads to a completely different property and a set of novel applications. Engineers and researchers are in a constant attempt to create novel nanomaterials or modify current ones to achieve many advantageous properties that were not available before. However, some of these properties that are desired from a technical point of view are undesirable and harmful to the environment and ecosystem. Therefore, there is a need for extensive toxicological research for this class of materials to avoid any possible risk and facilitate their safe implementation in future products. The first part of this chapter provides a short review on the

toxicity of some of the most important and commercially used nanoparticles utilized in polymeric nanocomposite production. Despite several research attempts focusing on the toxic behavior of nanomaterials, it has been seen there is no clear and solid understanding of their molecular scale mechanisms and proper procedures to prevent their adverse effect on the environment. It has been discussed that functionalization can increase or decrease nanomaterials' toxic effect depending on the nanomaterials' nature and surface functionalization type. The complex and in several cases the unknown toxic behavior of nanoparticles raises serious concern about their effect on human health and ecosystems and signifies the necessity of further scientific exploration and governmental regulations on their use. In addition, nanoparticle-based polymeric nanocomposites are a useful material class for a wide variety of applications that can promote human life and also serve our ecosystem. The replacement of conventional materials with their nanocomposite counterparts has increased the efficiency, lifetime, and reliability, and enabled several novel applications in various areas such as food packaging, membranes, and energy storage systems, among others. To reiterate, nanocomposites with their unique properties are key for further technological advancement in many areas. However, further multidisciplinary research is needed to evolve the understanding of their environmental effects and produce nanocomposites with minimum adverse effect on the ecosystem.

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Abstract

In the past decade, there has been a dramatic increase in the production and application of engineered nanomaterials and their polymeric nanocomposites. This steep increase in the quantities of nanomaterial raises the question of whether the unknown risks of engineered nanoparticles outweigh their benefits and what are the potential risks of such materials on our health and the environment. There are several research results available focusing on the nanomaterials' harmful potential such as the toxicological effect on living organs, and other adverse environmental effects. However, no clear guidelines exist to quantify these effects and to prevent unplanned environmental costs.

Therefore, it is necessary for research and industrial communities to engage in nanotoxicological research, risk assessment protocol development, and safe handling guidelines preparation to minimize the environmental consequences of nanoparticles. This chapter will focus on the environmental effects of nanomaterials, nanotoxicology, and their novel and innovative environmentally friendly applications.

Key words: Nanoparticles; polymeric nanocomposites; nanotoxicology; environment; nanocomposites application.

Queries and Answers

Query: Please check the edits made to the sentence: "Furthermore, it is observed ... effect on cells " and amend if necessary.

Answer: Modifications have been made.

Query: Please check the edits made to the sentence: " In addition to the toxicity ... with ZnO nanoparticles themselves" and amend if necessary.

Answer: Modifications have been made.

Query: Please check the edits made to the sentence: The state of the dispersion ... modification of particles" and amend if necessary.

Answer: it seems OK.

Query: Please provide full reference details for Refs. [9,50].

Answer: [9] J.S.M. Zanjani, S. Okan Burcu, Y. Menceloglu, M. Yildiz

M. Delville, A. Taubert (Eds.), Self-Healing Thermosetting Composites: Concepts, Chemistry, and Future Advances, Hybrid Organic-Inorganic Interfaces: Towards Advanced Functional Materials, Wiley (2017).(CH3) DOI: 10.1002/9783527807130.ch3

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Query: There are five parts (a) to (e) of Figure 14-2, but these are not defined in the caption. Please provide a definition for each part.

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