1

Introduction for Nanomaterials and Nanocomposites: State of Art, New Challenges, and Opportunities

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1.1

Chemistry of Nanoscience and Technology

Science uses methodologies from synthetic chemistry and materials chemistry to obtain nanomaterials in specific sizes and shapes, with specific surface properties, defects, and self-assembly properties, designed to accomplish specific functions and uses [1]. *Nanoscale* is usually defined as being smaller than 1/10th of a micrometer in at least one dimension; this term is also used for materials smaller than 1 μm. An important aspect of nanomaterials is the vast increase in the surface area to volume ratio, which incorporates the possibilities of new quantum mechanical effects in such materials. Suspensions of nanoparticles are possible because the interaction of the particle surface with the solvent molecules is strong enough to overcome differences in density, which usually results from a material either sinking or floating in a liquid. Nanoparticles often have unexpected visual properties because they are small enough to confine their electrons and produce quantum effects. Nanostructured materials are classified as zero-dimensional, one-dimensional, two-dimensional, three-dimensional nanostructures. Nanomaterials are materials that are characterized by an ultrafine grain size (<50 nm) or by a dimensionality that is limited to 50 nm. Nanomaterials can be created with various modulation dimensionalities as defined by Richard W. Siegel: zero (atomic clusters, filaments, and cluster assemblies), one (multilayers), two (ultrafine-grained overlayers or buried layers), and three (nanophase materials consisting of equiaxed nanometer-sized grains). Recently, researchers are using a modified CVD technique for the fabrication of 0D Nanostructured materials (NSMs) [2, 3].

Palgrave and Parkin [4] used the aerosol-assisted CVD technique to fabricate the Au nanoparticles on a glass substrate. Toluene is used as a precursor to deposit gold nanoparticles onto glass. The sizes of Au nanoparticles are 100 nm. Boyd *et al.* [5] developed a new CVD process that can be used to selectively deposit materials of many different types. In this technique, they used the Plasmon resonance in nanoscale structures to create the local heating, which is crucial in order to initiate deposition when illuminated by a focused low-power laser [6]. Elihn *et al.* [7] synthesized the iron nanoparticles enclosed in carbon shells by

Nanomaterials and Nanocomposites: Zero- to Three-Dimensional Materials and Their Composites,
First Edition. Edited by Visakh P.M. and Maria José Martínez Morlanes.

laser-assisted chemical vapor decomposition (LCVD) of ferrocene ($Fe(C_5H_5)_2$) vapor in the presence of the Ar gas. One-dimensional nanomaterials have nanoscale sizes along two-dimensions and a rod-like or wire-like appearance. In such nanomaterials, quantum confinement and surface area-related nanoscale effects are more pronounced compared to 2D nanomaterials. Lyotropic liquid crystal (LLC) template-assisted synthesis is one of the most facile and most applied methods for the synthesis of 1D NSMs such as nanowires, nanorods, nanotubes, nanobelts, nanoribbons, and nanospindles [8–12]. Kijima *et al.* [12] fabricated the platinum, palladium, and silver nanotubes, with inner diameters of 3–4 nm and outer diameters of 6–7 nm, by the reduction of metal salts confined to lyotropic mixed Liquid Crystals (LCs) of two different sized surfactants.

Electrodeposition processes have a wide range of advantages such as low cost, low energy consumption, high growth rate at relatively low temperatures, being environmentally friendly, and having good control of the deposition thickness, shape, and size. Xia *et al.* [13] fabricated the MnO_2 nanotube and nanowire arrays via an electrochemical deposition technique using porous alumina templates. Tang *et al.* [14] prepared the Si nanowires on Si substrates by the hydrothermal deposition route under low temperature and pressure. The obtained Si nanowire consists of a polycrystalline Si core and an amorphous silica sheath. The diameter and length of Si nanowires were 170 nm and 10 lm, respectively. The essence of nanoscience and nanotechnology is the creation and use of molecules, molecular assemblies, materials, and devices in the range of 1–100 nm, and the exploitation of the unique properties and phenomena of matter at this dimensional scale.

1.2
Carbon Nanotubes and Their Nanocomposites

Carbon nanotubes CNTs consist of tubes formed by rolled sheets of graphene (one atomic layer of graphite). The tubes are arranged in a concentric manner to form single-walled carbon nanotubes (SWCNTs), double-walled carbon nanotubes (DWCNTs) and multi-walled carbon nanotubes (MWCNTs). CNTs are excellent candidates for use in various applications: as biological and chemical sensors, as probe tips for scanning probe microscopy, in nano-electromechanical systems (NEMS), and as reinforcement in nanocomposites [15, 16]. CNTs consist of rolled graphene sheets arranged in a concentric manner and are classified according to the number of walls. The length of the nanotubes is between a few hundred nanometers and a few micrometers. Due to their length they become entangled. In general, the SWCNTs are defect-free, whereas MWCNTs present defects. An individual graphene sheet has high strength (130 GPa) and high electrical and thermal conductivities [17, 18]. Due to these remarkable properties, it is expected that since the CNTs consist of rolled graphene sheets, they will also exhibit extraordinary properties. CNTs have generated a great deal of interest in recent years.

The application of CNTs as a reinforcement is very important in any kind of matrix, but is more widely used in polymer matrix composites. The conventional polymer matrix composites have found application in a wide range of fields due to properties such as low density, reasonable strength, flexibility, and easy processability. However, the search for materials capable of improving the performance of advanced components has triggered the study and production of CNTs reinforced nanocomposites. CNTs/epoxy nanocomposites have been extensively investigated due to their industrial and technological applications. These nanocomposites are fabricated using melt mixing or solution mixing methods. Zhou *et al.* [19] demonstrated that it is possible to improve the strength and fracture toughness with the incorporation of 0.3 wt% CNTs in the epoxy matrix. Velasco-Santos *et al.* [20] studied the CNTs/PMMA (poly Methyl Methacrylate Monomer) nanocomposites and observed an increase in the storage modulus of 1135% for composites, with 1 wt% of CNTs dispersed using an *in situ* polymerization at 90 °C.

Ceramic matrices reinforced with CNTs can provide nanocomposites with super plastic deformability, high strength, improved fracture toughness, and higher electrical and thermal conductivities, while metallic matrices reinforced with CNTs are expected to produce nanocomposites of high strength and specific stiffness, which is a desirable coefficient of thermal expansion and good damping properties [21]. Yamamoto and Hashida [22] developed a new technique to obtain a more homogeneous dispersion of CNTs and improve the bonding to the alumina matrix. This treatment involved the use of a precursor method for the synthesis of an alumina matrix, MWCNTs modified by a covalent functionalization (by a concentrate H_2SO_4 and HNO_3 acid mixture), and the Spark Plasma Sintering (SPS) method. Nguyen *et al.* [23] showed that it is possible to produce ultrafine-grained MWCNT/Ni composites by the SPS method with 97% of density. The authors used modified CNTs by noncovalent functionalization to improve the cohesion between the CNT and Ni powders. The composites revealed a higher value of hardness in the CNT than the Ni. Kwon and Leparoux [24] obtained a higher strength for CNT/Al nanocomposites produced by mechanical ball milling followed by a direct powder hot extrusion process. The joining of the dispersion and mixture processes in a single step, by ultrasonication was effective in the formation of a uniform dispersion of CNTs through an Al matrix of the nanocomposites. CNTs are embedded in the grains of Al, which is essential for effective load transfer from the matrix to the reinforcement, and improves the mechanical properties of the nanocomposite.

1.3
Graphene- and Graphene Sheets-Based Nanocomposites

Graphene is extraordinarily strong (the strongest material ever known or tested), supernaturally light, and electrically super-conductive. It is 200 times stronger than steel, thinner than a sheet of paper, and more conductive than copper. Its flexibility and structure also make it the leading candidate as the primary component of next-generation, ultrahigh speed circuitry in everything from computers, to smart phones, to televisions. It is therefore of interest to a range of industries. Graphene CNTs can effectively stack transistors on top of one another on microchips, allowing for exponentially more transistors on a chip without increasing the size. More transistors means more operations per second, which in turn means more processing power and faster processing speed. Graphene sheets are composed of carbon atoms linked in hexagonal shapes with each carbon atom covalently bonded to three other carbon atoms. Each sheet of graphene is only one atom thick, and each graphene sheet is considered a single molecule. Graphene's electron mobility is faster than any known material and researchers are developing methods to build transistors on graphene that would be much faster than the transistors currently built on silicon wafers. Another interesting application of graphene that is being developed takes advantage of the fact that the sheet is only as thick as a carbon atom. Researchers have found that they can use nanopores to quickly analyze the structure of DNA. In the 1960s, Boehm speculated that reducing exfoliated graphite oxide would yield monolayers in solution [25], although the term *graphene* was not coined until 1986 [26] and was formally accepted only in 1994 [27]. A number of early studies, as early as van Bommel in 1975, found monolayers of carbon in graphitic structures, formed on various carbide [28] and transition metal [29] surfaces, with SiC [30].

Many methods of removing the oxygen from the graphene oxide (GO) structure through chemical, [31] thermal, [32] electrochemical [33], or electromagnetic flash [34], as well as laser-scribe [35] techniques have been successful, but have generally resulted in inferior samples and are hence more precisely named reduced graphene oxide (rGO). Nethravathi and Rajamathi described that chemically modified graphene sheets are obtained through solvothermal reduction of colloidal dispersions of graphite oxide in various solvents. Reduction occurs at relatively low temperatures (120 – 200 °C). Reaction temperature, the self-generated pressure in the sealed reaction vessel, and the reducing power of the solvent influences the extent of reduction of graphite oxide sheets to modified graphene sheets.

Graphene nanocomposites at very low loading show substantial enhancements in their multifunctional aspects, compared to conventional composites and their materials. This not only makes the material lighter with simple processing, but also makes it stronger for various multifunctional applications [36]. Jang and Zhamu reviewed the processing of graphene nanoplatelets (GNPs) for fabrication of composite materials [37]. Mack *et al.* prepared nanocomposites of polyacrylonitrile (PAN) nanofibers strengthened by GNP, which they demonstrated to have improved mechanical qualities [38]. Das *et al.* [39] employed the nanoindentation technique to the graphene-reinforced nanocomposites fabricated by using polyvinyl alcohol (PVA) and poly Methyl Methacrylate Monomer (PMMM). The results showed significant improvement in crystallinity, elastic modulus, and hardness through the addition of only 0.06 wt% of graphene.

1.4
Nanocomposites of Polyhedral Oligomeric Silsesquioxane (POSS) and Their Applications

The most common representation of zero-dimensional nanomaterials is polyhedral oligomeric silsesquioxane POSS nanoparticles, POSS-based compounds are thermally and chemically more stable than siloxanes. Of several structures of silsesquioxanes (random, ladder, and cage), cage structures contain eight silicon atoms placed at cube vertices. Cubic structural compounds are commonly represented based on the number of silicon atoms present in cubic structure. POSS is unique in the size (1.5 nm in core diameter) when compared to other nanofillers and can functionally tailor to incorporate a wide range of reactive groups [40]. POSS containing polymers received good attention during the last decade as a novel category of nanoscale-structured materials. Incorporation of bulky POSS particles into linear thermoplastic polymers can impart better organo-solubility because of the introduction of bulky POSS pendent group by decreasing the intermolecular forces between the polymer chains. Fina *et al.* [41] prepared the maleic anhydride-grafted polypropylene (PP-g-MA)/POSS hybrids by POSS grafting during a one-step reactive blending process. Polyamide 12/trisilanolphenyl–POSS composites were prepared via melt-compounding. The effect of POSS on crystalline structure and crystalline transition of PA 12 were studied and enhanced the tensile strength and thermal stability of PA 12 [42]. The POSS fractions in the nanocomposites were tailored by the PA–MI polymer maleimide contents and showed great influence on the thermal and mechanical properties of the polyamide–POSS nanocomposites [43]. Synthesis of liquid crystal POSS and specific problems connected with the nature of silsesquioxane cage, and special properties that their geometry imparts to their mesogenic behavior of liquid-crystal polyhedral silsesquioxane materials have been described [44]. POSS monomer (POSS-MA) was used as a novel dental restorative composites to replace commonly used dental base monomer 2,2′-bis-[4-(methacryloxypropoxy)-phenyl]-propane (Bis-GMA) [45]. Amino functionalized silsesquioxane provides curl retention for hair [46].

Polyfluorenes/POSS nanocrystal NC shows maximum luminescence intensity and quantum efficiency, which is almost twice as good as those of a Polytetrafluoroethylene (PFO EL) device, and is an excellent material for optoelectronic applications [47]. Castaldo *et al.* [48] presented polymeric NC sensors, based on a POSS by selecting a proper matrix such as poly[(propylmethacryl-heptaisobutyl-POSS)-*co*-(*n*-butylmethacrylate)] and a suitable choice of other external home-made fillers. Polyphenylsilsesquioxane is used as interlayer dielectrics and protective coatings films for semiconductor devices, liquid crystal display elements, magnetic recording media, and optical fiber coating.

Poly(aminopropyl silsesquioxane) and specific carbonyl compounds of silsesquioxane act as an antitumor agent. Silsesquioxane films, particularly OAPS/imide and OAPS/epoxide films, provide excellent O_2 barrier properties, and is an ideal candidate for packaging applications [49]. In Poly Vinyl Chloride (PVC), POSS behaves as a plasticizer like dioctyl phthalate (DOP) and could be used as a plasticizer [50]. Metal-containing POSS cages (gallium-containing cage silsesquioxanes and aluminosilsesquioxane) [51, 52] have been synthesized, for the use of silica-supported metal catalysts.

1.5
Zeolites and Composites

Zeolites are a series of crystalline microporous alumino silicates found on the earth's surface and in a number of environments, including soils, seafloor deposits, hydrothermal alteration products, altered volcanic deposits, sediments, and so on [53]. Zeolites find their application in sorbents, water purification, ion exchange beds, catalysts, optically active materials, polymerization science, separation technology, micro-electronics, photoelectrochemical applications in solar cells, thin-film sensors, and encapsulation of drugs and biomolecules for the targeted or controlled-release applications [54].

The significant advancements in zeolite synthesis were achieved by the utilization of organic components; specifically, the tremendous growth has been reported for the siliceous zeolites, and a number of new high-silica zeolites were successfully crystallized using organic cations with aluminosilicate gels at 100–200 °C. Koet al prepared the TiO_2/natural zeolite (TiO_2/NZ) composite from sol–gel derived nanotitania colloids and zeolite powder. Under vigorous magnetic stirring, natural zeolite was mixed with titania sol. The photophysical properties of zeolites are purely dependent upon the presence of cations in the zeolite framework and adsorbed water molecules over their surfaces [55]. Since the donor strength of guest molecules affects the absorption band of chromophores of strong electron acceptors, the optical property of chromophores can be effectively tuned by direct interaction with cations. The electrical properties of zeolites are associated with the composition and content variation of zeolite, pore size, and ion exchange capacity [56]. The movement of positive ions into the pore distribution along the zeolite varies the electrical conductivity. The location of charge balancing cations in zeolites exhibited excellent magnetic properties, owing to their unpaired electrons, influenced by the distribution of silicon and aluminum ions within the aluminosilicate framework [57].

The magnetic interaction of zeolite network depends upon the charged cations and the distance between the two charged species along the framework. Fuel cell is one of the most significant and outstanding electrochemical device in which the role of zeolites as catalysts and fillers in membranes is imperative. Zeolite serves as a better alternative to porous materials (employed in fuel cells), owing to its unique advantages including high electrical and thermal conductivity, high chemical and physical stability, extended surface area and porosity, low cost, and so on. The higher efficiency obtained is attributed to the lower methanol crossover as well as the excellent proton conductivity attained through the water up-taking ability of zeolites [58].

The lower methanol permeability obtained is attributed to the high diffusion resistance of the membrane achieved by the smaller pore size (0.3 A) and the inorganic nature of zeolites [59]. The improved performance of the anode was achieved by the higher surface area and porosity of zeolites for bacterial adhesion [60].

Boyas *et al.*, exploited the bifunctional Pt/zeolite (Pt-H-Y) as the catalyst in the hydrocracking of rapeseed oil. The time consumed by the Pt-H-Y catalyst for cracking the rapeseed oil is 3 h, which is lower than that of other catalysts. Zeolite-based photocatalysts are promising material for the abatement of air and water pollution by using solar light, photoreduction of CO_2 by H_2O, photo-oxygenation of saturated hydrocarbons, photosplitting of water into hydrogen and oxygen, photogeneration of hydrogen peroxide, and other photo processes [61]. Fukahori *et al.*, synthesized the TiO_2/zeolite sheets through papermaking technique and the prepared material was exploited as the photocatalyst in the degradation of bisphenol A (BPA). The TiO_2/zeolite sheets exhibited a higher efficiency for BPA removal than that of bare TiO_2 sheets. The higher efficiency obtained is ascribed to the reversible adsorption, the free movement of BPA molecules on composite attained by the cage-like structure, and the pore connectivity of zeolites [62].

1.6
Mesoporous Materials and Their Nanocomposites

Zeolites, the first primitive porous materials, were first discovered in 1756 by the Swedish scientist Axel Fredrik Cronstedt. Zeolites have aluminosilicate frameworks, which were synthesized via nonsurfactant-assisted route employing a single molecule template and having small micropores inside it. Among the above-mentioned materials, mesoporous materials are of specific importance due to their high stability, surface areas, and large pore volumes, which make them the most suitable candidates to be used as adsorbents, ion-exchangers, catalysts, catalyst supports, and in many other related applications [63].

Mesoporous materials prepared using neutral surfactants as templates possess improved stability. In case of primary amine (with carbon tail lengths between C_8 and C_{18}) as templates, the pore size of the final mesoporous silicas can be tuned by changing the hydrophobic tail length of amines. Preparation of mesoporous molecular sieves with large framework wall thickness, small particle sizes, and complementary framework confined and textural mesoporosity. In addition, the S_oI_o approach allows for cost reduction by employing less expensive reagents and mild reaction conditions while providing for the effective and environmentally benign recovery and recyclability of the template. The basic interest in mesoporous silica stems from the presence of a well-ordered structure that provides high surface area and accessibility to molecular species through the channels. In addition, the possibility of synthesizing different types of mesostructures with multiple pore architecture further enhances their versatility for different applications. In 1998, regarding the preparation of large-pore ordered mesoporous silica with a 2D hexagonal structure, Zhao *et al.* used triblock copolymers as templates, which is very famously known as *SBA-15* [64].

In 1998, a new family of highly ordered mesoporous silica materials has been synthesized in an acid medium by the use of nonionic triblock copolymers ($EO_nPO_mEO_n$) with large polyethyleneoxide (PEO) and polypropyleneoxide (PPO) blocks. Different materials with a diversity of periodic arrangements have been prepared and denoted as SBA materials (the acronym for Santa Barbara Amorphous) [65].

Synthesis of mesoporous metal oxides with high surface area, crystalline frameworks, and well-connected uniform pores is particularly important to achieve improved application performances. Similar to that for silica-based mesoporous materials, the synthesis of mesoporous metal oxides is mainly accomplished through the soft-templating approach. Ordered mesoporous materials with different compositions from pure inorganic or pure organic frameworks to organic–inorganic hybrid frameworks have been widely reported in the past two decades. For example, mesoporous metal oxides and mixed oxides with semicrystalline frameworks, such as TiO_2, ZnO, WO_3, SnO_2, and Al_2O_3 are successfully prepared by a direct synthesis strategy using amphiphilic copolymer templates. For the synthesis of mesoporous metal oxides by this structure replication procedure, a precursor compound, typically a metal salt, is filled into the pores of the silica matrix. The precursor compound is then converted into the metal oxide by thermal decomposition, sometimes preceded by a pH-induced conversion into an intermediate phase (such as a hydroxide species). Mesoporous carbon has been used as a potential matrix for the immobilization of biomolecules [66]. The widespread applications of porous carbons are attributed to their remarkable physicochemical properties, including hydrophobicity of their surfaces, high corrosion resistance, good thermal stability, high surface area, large pore volume, good mechanical stability, easy handling, and low cost of manufacture. Introduction of organic moieties within the silicate framework increases the flexibility of mesoporous films and fibers and reduces the brittleness of monoliths. Organic/inorganic hybrid materials are important because they can be designed at a molecular level to perform many processes including catalysis, adsorption, separation, drug delivery, and sensing. Mesoporous silica has a large surface area and a lot of constrained space in the form of nanochannels. Polymers grown within the constrained space of periodic mesoporous silica may exhibit unusual mechanical, electronic, magnetic, and optical properties. The spatial control of the growth process is limited by the channel network of the silica host, which allows the fabrication of materials with designed shapes, particularly nanofibers, wires, and porous particles. Mesoporous silica/polymer nanocomposites are synthesized with extrusion polymerization and are found with special properties [67]. The reason is that the nanoreactor gives space constraints on polymer chains when they grow inside the nanochannels. For example, polyethylene made with this method had ultrahigh molecular weight, high melting temperature, and only extended chain crystals rather than folded chain crystals because of the space constraint which controlled the formation of crystals. Mesoporous silica/polymer nanocomposites can also be made through entrapping polymers in the nanochannels of mesoporous silica through the hydrogen bonding between the silanol groups on the silica surface and the groups in the polymer chain. Mesoporous materials thus provide improved delivery systems for biomolecules, which have local and sustained release over time, while simultaneously protecting the biopharmaceutical agent from degradation. These delivery systems maintain the concentration of drugs in the precise sites of the body within optimum range and under the toxicity threshold, improve the therapeutic efficacy, and reduce toxicity [68].

1.7
Bio-Based Nanomaterials and Their Bio-Nanocomposites

Bio-based nanocomposites are composite materials that are made of particles from renewable natural sources and are in the range of 1 – 100 nm in size. These bio-based nanomaterials such as building blocks, particles, fiber, and resin, are combined to engineer a new material with enhanced properties. These new immerging "nano – bio" materials comprise exotic, dynamic, and fascinating features that make them smart futuristic biodegradable material. Cellulose is the most abundant polymer available in nature, after which comes hemicelluloses followed by lignin. This motivates scientists to discover new possibilities for biological materials in the rapidly expanding field of nanotechnology. Lignin has many different applications, including its use as a composite material. Hemicellulose has already been used for food applications but there are possibilities for new polymer production. Likewise, many researchers have also prepared nanoparticles using other natural compounds such as chitosan, dextran, gelatin, alginate, albumin, and starch [69 – 74].

The cellulose nanocrystals (CNCs) are rod-like or whisker-shaped particles with transverse dimensions as small as 3 – 30 nm, providing a high surface to volume ratio, also called cellulose nanowhiskers (CNWs). These particles have also been named nanocrystalline cellulose, cellulose whiskers, cellulose nanowhiskers, and cellulose microcrystals. Nanocellulose composites offer new possibilities for unaccountable applications in day-to-day life. Unlike cellulose, nanostructured cellulose provides a large variety of options for Chemistry and engineering for many material applications. Fundamental domain structures with high intrinsic strength, high melting temperature, directional rigidity, and ease of chemical modification can provide high reinforcement and scaffolding in the formation of nanocomposites [75, 76].

Chitin $(C_8H_{13}O_5N)_n$ is one of the widely available natural polymers on earth and functions naturally as a structural polysaccharide similar to the cellulose in plants and collagen in animals. Chitin and Chitosan (CS) and their derivatives are highly eco-friendly and nontoxic and nonallergic. They also possess good biodegradability, bioactivity, biocompatibility, coating ability, and good miscibility. Because of their nonantigenic properties, they are highly compatible with animal as well as plant tissues. Chitin/chitosan has been studied as a natural cationic biopolymer because of its excellent biocompatibility, biodegradability, nontoxicity, antimicrobial capability, and stimulation of wound healing [77]. Both chitin and chitosan materials have found applications as components in different products and processes [78, 79].

The hydrophilic nature of starch is a major constraint that seriously limits the development of starch-based nanoparticles [80]. A good alternative to solve this problem is the grafting of hydrophobic side chains to the hydrophilic starch backbone [81]. Various synthetic methods for synthesis of starch nanoparticles such as high-pressure homogenization and miniemulsion cross-linking, precipitation/nanoprecipitation [82] emulsion [83, 84], and microemulsion [85] have been explored by researchers. Ma *et al.* [86] have prepared starch nanoparticles by precipitating a starch solution within ethanol as the precipitant. Spherical or oval-shaped nanoparticles (diameters in the range of 10–20 nm) were prepared by the starch–butanol complex precipitation method [87].

Thus, starch bio-nanocomposites are of much academic as well as industrial interest. Most work has been oriented toward the use of new environmentally friendly polymers with starch nanocomposites such as natural rubber [88], waterborne polyurethane [89], waxy maize starch [90], cassava starch [91], pullulan [92], Poly Lactic Acid (PLA) [93], PVA [94], and soy protein isolate (SPI) [95].

1.8
Metal–Organic Frameworks (MOFs) and Their Composites

Metal–organic frameworks (MOFs) represent a class of crystalline and highly porous hybrid materials obtained by the assembly of metallic ions and organic ligands. MOFs exhibit interesting properties for gas separation, gas storage, and drug delivery and could also be used as sensors. Synthetic polymer–MOF composite membranes have been investigated using a polyimide (Matrimid) and a polysulfone polymer as the matrix. Composite membranes of MOF-5 and ZIF-8 (Zeolitic Imidazolate Framework) with Matrimid were prepared by the solution blending approach [96, 97]. Better quality composite membranes were formed by pretreatment of the MOF crystals with the silylating agent *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide. In a similar study, ZIF-8-polysulfone membranes were also obtained by the solution blending approach. The CO_2 diffusion properties of the composite membranes were studied, and the ZIF-8 crystals were shown to improve the transport of the gas through the membrane.

The monodisperse MOF–silica composites were tested as the High-Performance Liquid Chromatography (HPLC) stationary phase and showed good separation properties. In another report [98], silica and SiO_2/Al_2O_3 composite beads were used. Two methods were employed: formation under solvothermal conditions and immersion of the beads into preheated crystallization solutions. Recently opened new possibilities of applications are MOFs [99]. Yaghi and Li [100] were the first to describe the synthesis and properties of MOFs. In recent years, it has been shown that a large variety of 2D and 3D metal–organic networks with high porosity, unusual ion exchange, and adsorptive properties can be designed using intermolecular interactions and metal–ligand co-ordination [101].

The intercalation of graphene in MOF imparts new electrical properties such as photoelectric transport in the otherwise insulating MOF. The results point to the possibility of using functionalized graphene to synthesize a wide range of structural motifs in MOF with adjustable metrics and properties. Many research efforts have focused on these issues and the deposition of MOF on various supports such as alumina, silica, functionalized self-assembled monolayer (SAM), functionalized graphite, graphite oxide (GO), or amorphous carbon have been recently reported as a way to produce MOF-based membranes or composites. The porosity of the hybrid materials is in the range of that of the MOF; however, a slight decrease is found (except for MGr5) due to the addition of low- or nonporous graphite.

The results indicate that the oxidation of graphite is important to build MOF/graphite hybrid materials with synergistic properties. The presence of functional groups on the substrate's surface enables the formation of bonds between the components and thus the composites can be formed. The results suggest that MOF/graphite hybrid materials represent a distorted physical mixture of MOF and graphite. Besides the chemical features of the graphite, the physical parameters, and especially the porosity and size of flakes, also seem to influence the formation of the hybrid materials. Most MOF materials still show relatively low CO_2 and CH_4 uptakes. To enhance CO_2 and CH_4 adsorption, it is imperative to develop new materials such as covalent organic frameworks (COFs) or to modify MOFs by using postsynthetic approaches.

One of the modification approaches is incorporation of CNTs into MOFs in order to achieve enhanced composite performance, because of the unusual mechanical and hydrophobicity properties of CNTs. Another approach is doping MOFs or COFs with electropositive metals. Recent studies indicate that the surface carboxylate functional groups of a substrate could act as nucleation sites to form MOFs by heterogeneous nucleation and crystal growth. MOFs have been evaluated as promising H_2 storage media as MOFs exhibit exceptionally high surface areas and tunable pore size. An additional advantage of MOFs is that preparation is economic as MOFs are synthesized by "one-pot" solvothermal methods under mild conditions. The large surface areas, low framework densities and high pore volumes of MOFs compared to other porous matrices have motivated a great deal of interest in these materials, which have significant potential for use in a variety of applications ranging from storage of gases to application in heterogeneous catalysis [102–104].

In particular, externally accessible nanosized cavities and channels allow for the incorporation of substrates inside the crystal to facilitate the heterogeneous catalytic action of these MOFs. In the past decade, MOFs have received much attention due to potentially useful properties. As a new type of functional materials, the exceptionally high crystallinity and designability of MOFs can also open the door for investigation of the mechanism as well as for the functional regulation of proton conductivity. In general, some specific physicochemical properties of MOFs are controlled and modified by the judicious selection of organic ligands and metal centers. In conclusion, micropore- and mesopore-integrated materials have been synthesized by using mesoporous silica and MOF. The composites were composed of nano-CuBTC (Copper Benzene 1,3,5 tricarboxylic acid) crystals and mesoporous silica, and the ratio of micropore/mesopore volume can be tuned by controlling the initial concentration of the reaction solution of CuBTC. Under synthesis in low-concentration solution of CuBTC, the obtained composites showed higher adsorption uptake than the estimated uptake of MOF–mesoporous silica mixture showing the retention nature of micro- and mesoporous materials and formation of additional pore spaces that should be from the space between the nano-CuBTC crystals.

The MOFs are a class of the nanoporous materials. MOFs are most attractive for their high capacity for hydrogen absorption and storage, capture and separation of gases, and for applications in catalysis.

1.9

Modeling Methods for Modulus of Polymer/Carbon Nanotube (CNT) Nanocomposites

The CNT-reinforced nanocomposites are applied in a wide range of aerospace structures, automotive components, sporting goods, conducting plastics, electromagnetic interference shielding, optical barriers, biomaterial devices, and different sensors [105]. The mechanical properties of polymer nanocomposites depend on many parameters such as aspect ratio (α), alignment, waviness, dispersion, and agglomeration of nanoparticles as well as on the interaction between polymers and nanofillers [106–110].

The mechanical properties can be predicted by various computer modeling methods at large scales of length and time from molecular, microscale to macroscale, and their combination as multiscale techniques. Molecular modeling is a powerful instrument to study the atomic structure and interaction at the nanometer scale [111]. This approach assumes a noncontinuous organization of material wherein its discrete nature often limits the length and time scales. The commonly used techniques of molecular modeling for mechanical properties of polymer/CNT nanocomposites are molecular dynamics (MDs) and molecular mechanics (MMs) [112]. Molecular dynamics is the most widely used modeling technique that allows the accurate prediction of an interaction between constituent phases at the atomic size [113].

Griebel and Hamaekers [114] have shown an excellent agreement between MD results with rule of mixtures and extended rule of mixtures models for extremely long and short CNTs. The MD simulation of polystyrene (PS)/CNT nanocomposites exhibited that the ion beam deposition modification produces many cross-links between CNT and polymer chains which reinforce the nanocomposites [115]. The optimum condition for this sample was observed in high ion energy and compact structure. Using molecular mechanics simulation, Mokashi *et al.* [116] found that the length of CNTs and the configuration of polyethylene (PE) play an important role in the tensile properties of nanocomposites. The crystalline PE caused a moderate improvement by long CNT, while the short CNT caused a significant reduction in the modulus of amorphous PE resulted from a poor load transfer at the interface.

Huang *et al.* [117] considered the 3D end effects of SWCNT by introduction of a length factor. Their model can be applied for a CNT loading between 0 and 5 vol%, while the Finite element method (FEM) model is suitable for a CNT content about 5 vol% [118]. Song and Youn [119] also used the asymptotic expansion homogenization method to perform both localization and homogenization for a heterogeneous system. They found a good agreement between the numerically and the analytically calculated elastic moduli.

The calculated modulus by M-T for PET/SWCNT (Poly ethylene teriphtalate) nanocomposites [120] has been higher than the experimental results. Ogasawara *et al.* [121] also studied the effect of 3D random orientation and entangled distribution of CNTs in polyimide/MWCNT nanocomposites, conducted based on the Eshelby–Mori–Tanaka theory. Coleman *et al.* [122] stated that the substantial increment of modulus in polymer/CNT nanocomposites is attributed to the formation of an ordered polymer layer around the CNT. The nucleation of this layer increases the crystallinity of polymer, which improves the stiffness of nanocomposites. Guzman de Villoria and Miravete [123] also introduced a new micromechanics model called the dilute suspension of clusters taking into account the influence of inhomogeneous dispersion of nanofillers in nanocomposites. The proposed model significantly improved the theoretical–experimental relationship for epoxy/clustered CNT nanocomposites.

Fisher *et al.* [124] studied the effect of the wavelength ratio of the CNT on the modulus assuming the minimal CNT waviness distribution ($0 < w < 1$) and the more moderate waviness ($0 < w < 1$). Bradshaw *et al.* [125] also predicted the effective modulus of nanocomposites containing aligned or randomly oriented CNT. Furthermore, Shao *et al.* [126] proposed a model to calculate the effect of CNT curvature and interfacial bonding on the effective modulus of nanocomposites. They found that the modulus is very sensitive to waviness and this sensitivity falls with the enhancement of waviness.

1.10
Nanocomposites Based on Cellulose, Hemicelluloses, and Lignin

Cellulose is considered to be the most ubiquitous and abundant biopolymer on the planet, which has been used for many centuries as a construction material, in the forest products, as natural textile fibers, as paper and boards, and so on. *Cellulose* is defined as a linear β-1,4-linked homopolymer of anhydroglucose or, more recently as a homopolymer of anhydrocellobiose [127]. The intramolecular hydrogen bonds are responsible for the stiffness of the chain and stabilize the twofold helix conformation of crystalline cellulose [128]. The intermolecular hydrogen bonding in cellulose is responsible for the sheet-like nature of native cellulose. The term *cellulose nanoparticles* generally refers to cellulosic particles having at least one dimension in the nanometer range [129]. On the basis of the cellulosic source and the processing conditions, cellulose nanoparticles (CNs) may be classified into three main subcategories, as nanofibrillated cellulose (NFC), CNCs, and bacterial nanocellulose (BNC).

Generally, the main extraction processes in the preparation of CNs are mechanical treatment and acid hydrolysis. Mechanical processes can be divided into high-pressure homogenization and refining [130], microfluidization [131], grinding [132], cryocrushing [133], and high-intensity ultrasonication [134].

In recent years, CNs-based nanocomposites have been extensively used in different areas such as food packaging materials, [135], optical, light-responsive composites and other electronic devices [136], as well as in advanced composites manufacturing [137], printing and paper industry, and pharmaceutical and medical applications [138]. As biomedical application, the CNs-based nanocomposites are used as scaffolds in artificial ligaments or tendon substitutes, due to their excellent cytocompatibility [139].

Hemicelluloses represent an important renewable resource of biopolymers, but their utilization for the achievement of new materials is rather limited. Moreover, the procurement of hemicelluloses in their pure form is still challenging. These constitute about 20–30% of the total mass of annual and perennial plants and have a heterogeneous composition of various sugar units classified as xylans (β-1,4-linked D-xylose units), mannans (β-1,4-linked D-mannose units), arabinans (α-1,5-linked L-arabinose units), and galactans (β-1,3-linked D-galactose units) [140]. Wide variations in hemicelluloses content and chemical structure can occur depending on the biomass type, that is, maize stems (28.0%), barley straw (34.9%), wheat straw (38.8%), and rye straw (36.9%) [141] or on the components of an individual plant, that is, stem, branches, roots, and bark [142].

Considerable interest has been directed to hemicelluloses-based biomaterials due to their nontoxicity, bio-based origin, bioactivity, biocompatibility, and oxygen barrier properties, which give them potential in numerous applications, such as drug delivery, tissue engineering, and food packaging. Among these research activities, hemicellulose-based films have received ever-increasing interest as oxygen barrier films, but suffer from low film-forming ability and mechanical performance. An effective and simple method to produce hemicelluloses-based nanocomposite film of high quality was proposed by Peng *et al.* [143] who incorporated cellulose nanofibers (CNFs) into xylan (XH) films in the presence of plasticizers. The sugar composition (relative weight percent) by the sugar analysis is: 89.38% xylose, 5.75% arabinose, 1.87% glucose, 0.66% galactose, 1.78% glucuronic acid, and 0.55% galacturonic acid.

The freeze–thaw technique was used by Guan *et al.* [144] to prepare a novel hybrid hydrogel from hemicelluloses extracted from bamboo (*Phyllostachys pubescens*) holocellulose, PVA, and chitin nanowhiskers. Lignin, the main aromatic component of vegetable biomass, presents a special interest both due to its vast reserves, which are still less valorized, as well as due to its active role in the complex process of organic material formation and conversion in biosphere.

Several studies revealed that similar functional groups are found in all types of lignin [145]. Thus, softwood lignin contains guaiacyl propane units that include a methoxy group bonded to the third carbon atom of the aromatic ring, while hardwood lignin has guaiacyl propane units and syringyl propane units.

The main advantage of the hydroxymethylated lignin is its high content of hydroxyl groups, which allows for its use as a phenol substitute in phenol formaldehyde resin synthesis [146], composites, biocides systems, and bioremediation [147].

Nevárez *et al.* [148] prepared biopolymer nanocomposite films by vapor-induced phase separation at controlled temperatures (35–55 °C) and relative humidity, RH (10–70%) using lignin as a filler and cellulose triacetate (CTA) as a polymer matrix. Lin *et al.* [149] showed that enzyme-hydrolyzed lignin content affected the structure and properties of the PANI–lignin (Polyanilene) nanocomposites.

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