CHAPTER: I

INTRODUCTION

1.1 Introduction to nanotechnology and nanomaterials

Nanoscience and nanotechnology refer to the science and technology of matter, manipulated at the atomic level. It is an area in which traditional disciplines converse. The word "nano" is derived from the Greek term meaning "dwarf," indicating something extremely tiny. In scientific terms, it represents one billionth of a unit, specifically 10^{-9} meters. Nanotechnology is an expanding research domain that focuses on particles with dimensions on the nanoscale, which have diverse applications across different areas of science and technology [1]. Nanotechnology has the potential to transform human's life through its extensive applications in energy production and storage, information technology, medicine, food safety, equipment manufacturing, and environmental science [2, 3]. This transformative capability arises from the unique physicochemical properties of nanomaterials compared to larger-scale counterparts. These properties are primarily due to the increased surface area and energy associated with smaller particles, which leads to different behaviors and interactions in comparison to bulk materials [4, 5].

Physicist Richard Feynman gave a pioneering lecture on December 29, 1959 titled "There's Plenty of Room at the Bottom" to the American Physical Society, which focused on the potential of nanomaterials [6]. In his lecture, he not only advocated for the use of nanomaterials in information storage but also introduced various innovative techniques that laid the groundwork of nanotechnology. Since Feynman's lecture, materials with sizes between 1 and 100 nm have been referred to as nanomaterials. It has gained prominence due to advancements in research methodologies that enhance both theoretical and experimental understanding. One of the remarkable aspects of nanomaterials is that their properties can be dramatically altered by simply reducing size, all while maintaining the same material composition. In contrast to nanomaterials, bulk materials are defined as those with sizes exceeding 100 nm. The physical properties of bulk materials remain constant regardless of size, while the characteristics of nanomaterials can vary significantly based on their size and shape. Thus, advancements in materials research are largely reliant on nanoscience and nanotechnology for the creation of functional nanomaterials aimed for advanced applications [7, 8].

1.2 Classification of nanomaterials

Nanomaterials are categorized based on their morphology, chemical composition, shape and size, state, and dimensionality. Figure 1.1 provides a comprehensive classification, which is further outlined in the summary below.

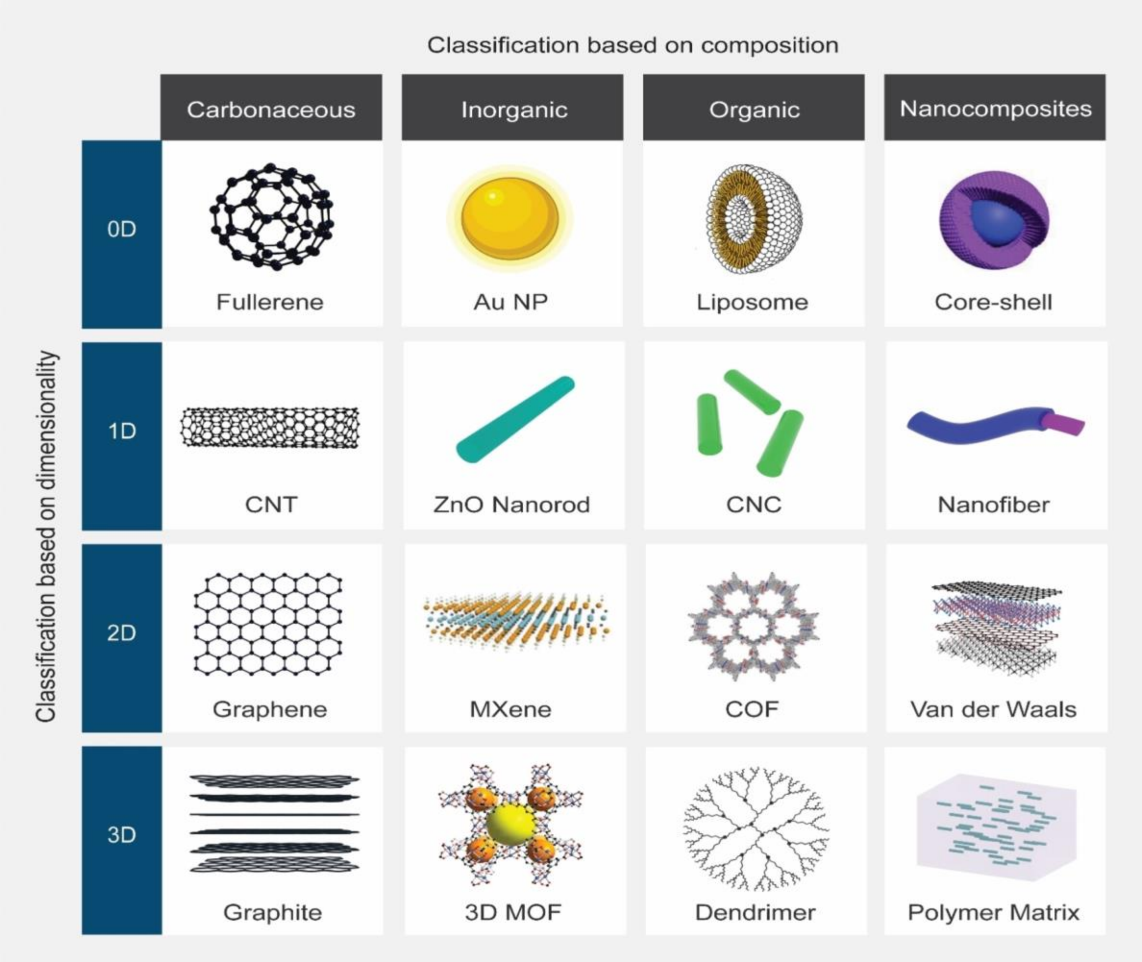

Figure 1.1 Classification of nanomaterials [8]

1.2.1 Classification based on dimensionality

(a) Zero-dimensional nanomaterial

Zero-dimensional nanoparticles are defined by their extremely small size, with all dimensions measuring less than 100 nm. Common examples include quantum dots (typically under 10 nm), nano lenses, hollow spheres, and fullerenes [9]. A key property of these materials is their semiconductor nature, which allows them to utilize in electronics for confining electric holes.

(b) One-dimensional nanomaterial

One-dimensional nanoparticles have one dimension exceeding 100 nm, while the remaining dimensions are within the nanoscale (below 100 nm). Examples include nanofibers, nanotubes, nanorods, and nanowires [10] .

(c) Two-dimensional nanomaterial

Two-dimensional nanomaterials possess two dimensions that exceed 100 nm, while the thickness is at the nanoscale. Examples include nanofilms, nanocoatings, and nanolayers etc. These materials typically exhibit plate-like structures [10].

(d) Three-dimensional nanomaterial

Three-dimensional nanomaterials possess all three dimensions measuring more than 100 nm. These materials are formed by the aggregation of nanoscale particles and are generally nonporous. Common examples include nanocomposites, bundles of nanofibers, and multilayer structures [10].

1.2.2 Classification based on morphology and state

Nanoparticles (NPs) can be classified according to their morphological characteristics, such as sphericity, flatness, and aspect ratio. Additionally, NPs can be categorized based on their dispersion and uniformity into two main types: inhomogeneous and isometric (or agglomerate), dispersed NPs.

1.2.3 Classification based on chemical composition

(a) Organic based nanomaterials

Organic-based nanomaterials are made up of organic compounds, excluding carbon and inorganic substances. They are created either by self-assembly or by converting organic matter into the target structure, depending on weak (noncovalent) interactions [4].

(b) Inorganic based nanomaterials

These nanomaterials are mainly composed of metals and metal oxides. It can be produced using metals like iron (Fe), gold (Au), and silver (Ag) etc, along with metal oxides such as manganese dioxide (MnO_2), zinc oxide (ZnO), and titanium dioxide (TiO_2) etc [10].

(c) Carbon based nanomaterials

Carbon-based nanomaterials (CBNs) are composed of carbon atoms arranged in different structures, including carbon quantum dots (CQDs), graphene, carbon nanofibers (CNFs), carbon nanotubes (CNTs), fullerenes, and other related forms. Some of the techniques used for synthesizing carbon-based nanomaterials includes chemical vapor deposition (CVD), laser ablation, arc discharge, etc [4].

(d) Composite based nanomaterials

Composite nanomaterials are formed by integrating one or more layers of nanoparticles with other nanoparticles, bulk materials, or intricate structures such as metal frameworks. These composites can incorporate a variety of materials, including metals, ceramics, organic, inorganic, carbon-based substances, or bulk polymers. Their morphology varies depending on the synthesis methods used and the specific properties required for their intended applications [11].

1.3 Introduction to nanocomposite

The word "nanocomposite" (NC) was originally coined by Blumstein in 1961 [12]. The early investigation of basic nanocomposites in 1965 focused on improving the thermal stability of nano-silicate reinforced polymethyl methacrylate (PMMA) [13]. The discovery of NCs featuring fillers with at least one nanoscale dimension was reported by Toyota Central R&D Labs., Inc. in Japan, demonstrating that nylon6/clay NCs exhibited notable improvements in mechanical and thermal properties. In general, composite material is defined as a combination of two or more materials with different properties, resulting in a material that exhibits improved characteristics compared to its individual components [14]. Typically, composite materials consist of one or more discontinuous phases dispersed within a continuous phase, referred to as the "matrix," while the discontinuous phases are known as "reinforcement" or "reinforcing materials." NCs share terminology with conventional composites regarding their constituents, but differ primarily in the size of the reinforcement, which typically ranges in the hundreds of nm. This shift from micro-sized to nano-sized fillers allows for significant reinforcement with a much lower filler content, leading to inconsiderable reduction in weight [15].

The key distinction between NCs and conventional composites lies in the fact that the reinforcing materials in NCs possess a significantly higher surface-to-volume ratio due to their nanoscale dimensions [9]. These reinforcing materials can take the form of particles, sheets, or fibers. Moreover, the interface area between the matrix and reinforcement in NCs is typically significantly greater than that in conventional composites. The properties of the matrix material are also significantly influenced by the reinforcing material. The effectiveness of nanocomposite materials relies not only on the characteristics of individual components but also on their structural arrangement and the interactions at their interfaces. With their exceptional attributes, NCs offer a promising substitute for micro composites and monolithic materials. Thus, it has attracted considerable interest from scientists and engineers across various fields, including biomedical applications, energy, environmental technologies, food industries, and automotive sector [12].

1.3.1 Classification of nanocomposites

Nanocomposites can be broadly categorized into three main types [16].

(a) Metal and metal-oxide based nanocomposites, (b) Ceramic-based nanocomposites and (c) Polymer-based nanocomposites

(a) Metal and metal-oxide based nanocomposites

These consist of heterogeneous nanoparticles, which include metal oxides, and noble metals. Metal-based NCs often exhibit enhanced mechanical, optical, electronic, optoelectronic, magnetic, and biomedical properties compared to single-component nanoparticles. This improvement is attributed to the synergistic effects occurring at the interfaces between different components, such as noble metals and metal oxides or between various metal oxide semiconductors. Notable examples of properties derived from metallic nanoparticles include electrical conductivity from gold (Au), antibacterial properties from silver (Ag), and magnetic properties from iron oxide (Fe_3O_4, Fe_2O_3) and zinc oxide (ZnO) etc. The combined effects of these materials can be further explored through the creation of binary, ternary, and quaternary NCs, with binary and ternary types being particularly suitable for biomedical applications. Binary nanocomposites may include combinations like metal oxide with nano metals or quantum dots, while ternary and quaternary NCs involve additional components to enhance properties for advanced applications [16].

(b) Ceramic based nanocomposites

Ceramics are versatile materials composed of non-metallic elements. Niihara *et* al. introduced the term "ceramic nanocomposites" during his innovative work on creating alumina oxide NCs using a chemical vapor deposition process [17]. A significant limitation of ceramics is their inherent brittleness, which restricts their applicability in many practical scenarios [16]. To address this issue, extensive research has been conducted to develop an advanced generation of ceramics by integrating secondary phases, such as particles, fibers, or whiskers. These additions enhance the material’s ability to withstand flaws by mitigating or redirecting cracks and stress. One of the most notable advancements in this field is the creation of ceramic NCs, where multiple phases are uniformly dispersed at the nanoscopic level within the ceramic matrix. These NCs possess improved mechanical strength, thermal stability, biocompatibility, and functional properties, making it ideal for biomedical, aerospace, automotive, and environmental applications. Some of the examples of ceramic reinforcements are Alumina (Al_2O_3), Titania (TiO_2), Silicon Carbide (SiC), Zirconia (ZrO_2), Hydroxyapatite (HA) etc.

(c) Polymer based nanocomposites

Polymer-based NCs are materials consisting of a polymer matrix that acts as a host, combined with nanofillers (such as nanotubes, graphene oxide, reduced graphene oxide, double-layered hydroxides, metal or metal oxide nanoparticles, clays, silica etc) that serve as reinforcements. Polymers exhibit several desirable characteristics, including lightweight nature, ease of processing, chemical resistance, ductility, affordability, as well as gas barrier, heat resistance, and fire resistance properties [16]. However, their primary limitation lies in their low thermal and electrical conductivities. Incorporating nanofillers into the polymer matrix as reinforcing agents significantly improves the limitations of the resulting polymer nanocomposite. The advancement of high-performance polymer nanocomposites depends on several key factors, including the shape, dispersion, morphology, and external stimuli affecting the nanofillers [7]. The choice of a suitable reinforcement material depends on the specific application for which it is intended. Additionally, several factors play a crucial role in enhancing the polymer matrix, such as (i) the type of polymer matrix, (ii) the nature and concentration of the nanofillers, and (iii) the average particle size, orientation, and distribution. Optimal material properties attained by incorporating excessive loading of nanofiller often leads to aggregation within the polymer matrix. Therefore, establishing a strong interfacial interaction with the polymer matrix is crucial to minimize aggregation at higher concentrations or to improve properties even when using lower amounts of nanofiller [16]. These NCs thus show enhancement in mechanical strength, thermal stability, barrier properties, and electrical conductivity for its diverse application in aerospace and automotive components, electronic devices, packaging, coatings and biomedical applications. Some of the common examples of polymers are polypropylene (PP), polyethylene (PE), epoxy, polycarbonate (PC), polyvinyl alcohol (PVA), polystyrene (PS), polylactic acid (PLA), cellulose etc.

1.4 Introduction to graphene and its derivatives

Graphene is a new class of material made up of a one-atom-thick layer of carbon atoms arranged through sp^2 hybridization. This two-dimensional (2D) structure consists of densely packed carbon atoms organized in a hexagonal honeycomb like crystal lattice [18]. The remarkable properties of graphene exhibit from the delocalized 'p' orbitals that create 'p state' bands across the carbon sheet. Theoretical investigations into graphene's unique electronic structure began in the year 1947 by physicist Philip R. Wallace, when it was recognized as an ideal subject for solid-state physics calculations. The term "graphene" was first used in the late 1980s to refer to individual sheets of graphite. For many years, graphene was thought to be non-existent in a free state and was regarded merely as a theoretical concept until 2004, when (Novoselov *et.* al) at Manchester University successfully isolated a one-atom-thick sheet of graphene from bulk graphite [19]. They accomplished this by using a technique known as micromechanical cleavage, or the "scotch tape technique," which involved repeatedly exfoliating graphite with adhesive tape to separate the layers. This process yielded mono, bi, or few-layer of graphene sheet.

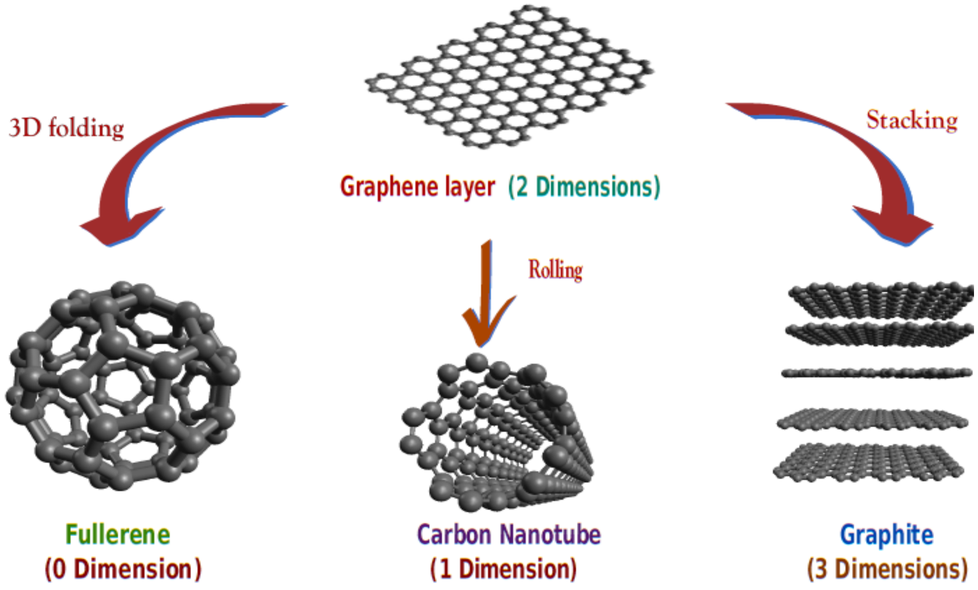

Figure 1.2 Graphene and its derivatives [20]

Single-layer or few-layer graphene sheets serve as parent compounds for various carbon allotropes, including fullerenes (0D structures), carbon nanotubes (1D structures), and stacked layers forming 3D graphite. Single graphene sheets exhibit remarkable properties, including a high surface area, the hall effect at room temperature, a tunable bandgap, and exceptional electrical and thermal conductivity (Geim and MacDonald, 2007) [21]. In graphene, the distance between adjacent carbon atoms is about 1.42 Å. The impressive performance of graphene is attributed to its outstanding characteristics with tensile strength (TS) of 130 GPa [22], thermal conductivity of 5000 W/m^{3}K [23], electrical conductivity up to 6000 S/cm [24], transparency of about 97.7%, specific surface area of 2630 m^2/g, Young's modulus (YM) of 1100 GPa, breaking strength of 125 GPa, theoretical surface area (up to 2630 m^2/g) [16] and its gas impermeability suggest potential applications in advanced applications [25]. Due to these fascinating properties, graphene has emerged as a prominent research area in today's scientific community. Figure 1.2 shows the different classification of graphene and its derivatives.

1.4.1 Graphene oxide

Graphene oxide (GO), also known as graphite oxide or graphitic oxide, is an organic macromolecule composed of wrinkled two-dimensional carbon sheets. It contains hydroxy and epoxy functional groups on the basal plane, while carboxyl groups are positioned at the edges. GO has garnered significant attention due to its hydrophilicity and the ease of modification offered by its numerous oxygen-containing functional groups [26]. The oxidized form of graphene, GO was first synthesized in 1859 by B.C. Brodie and later recognized in the scientific community as a precursor to graphene [27]. During the pre-treatment process, the sp^2 structure of graphite layers is disrupted, leading to the formation of various oxygen-containing functional groups, including epoxy, carboxyl, and hydroxyl groups [28]. Oxidation increases the interlayer distance in graphite due to the incorporation of these functional groups, primarily saturated closed rings. This oxidation process allows for the exfoliation of graphite oxide layers, resulting in a suspension of GO layers. The chemical heterogeneity of GO sheets is significantly influenced by factors such as the degree of oxidation and temperature [20]. The distinct structure and the presence of oxygen-containing functional groups, GO demonstrates outstanding thermal, mechanical, electronic, optical, and electrochemical characteristics. GO possess exceptional mechanical characteristics, including a TS of 130 GPa and YM of 0.25 TPa [29]. Unlike pristine graphene, which does not interact well with organic polymers and fails to form homogeneous composites, the tunable oxygen-containing groups in GO facilitate strong interactions with polar molecules or polymers. This property allows the formation of GO-intercalated or exfoliated composites. Consequently, GO has attracted considerable interest as a nanofiller for polymer nanocomposites. Numerous GO based polymer composites have been developed, demonstrating its diverse applications in electronic and energy storage, advanced composites and coatings, biomedical and food industries [16].

1.4.2 Reduced graphene oxide

Reduced graphene oxide (rGO) is derived from graphene oxide by reducing oxygen-containing functional groups, resulting in properties that closely resemble those of pristine graphene. The properties of rGO vary based on the degree of reduction; the greater the reduction, the more similar it becomes to graphene. This partially reduced form of graphene oxide has a recovered π-conjugated system, but still contains some residual oxygen and structural defects. Various methods, including thermal annealing, chemical reduction, electrochemical reduction, and hydrothermal reduction, are employed to convert GO into rGO [30]. For chemical reduction, common reducing agents include hydrazine, metal hydrides or hydrohalic acids [31]. Thermal reduction typically occurs at temperature range 300 °C to 2000 °C in an inert or reducing atmosphere. During this process, saturated oxygen functional groups are removed from the GO layers, leading to the restoration of conjugation. The reduction process significantly enhances the electrical conductivity along with gain in surface area of rGO. The mechanical strength of rGO is impressive as well, with a YM around 1.0 TPa and a breaking strength of approximately 130-150 GPa, making it comparable to graphene [30]. Unlike GO, rGO exhibits hydrophobic behavior due to an increased carbon-to-oxygen (C/O) ratio in its structure. This hydrophobicity reduces the dispersibility of rGO after reduction and affects its colloidal behavior by decreasing the critical coagulation concentration. Although the structure of graphene is not fully restored during the reduction of GO, rGO retains its valuable properties such as controllable functionality, high electrical and thermal conductivity, alongside a cost-effective and scalable preparation process.

1.4.3 Application of graphene and its derivatives

Graphene holds immense potential for a wide range of applications owing to its exceptional mechanical strength, electrical conductivity, and thermal stability. It is utilized across diverse fields such as energy storage, electronics, sensors, advanced coatings, nanocomposites, and biomedical devices. Its large surface area and biocompatibility make it especially attractive for drug delivery systems and tissue engineering also. These remarkable properties position graphene as a key material for many emerging technologies, as outlined below [14,30].

(a) Graphene applications in energy industry

Solar cells, fuel cells, nuclear power plant, alcohol distillation, thermoelectric etc.

(b) Graphene applications in medicine

Drug and gene delivery, cancer treatment, photo thermal and cell therapy, bone and teeth implantation, tissue engineering, biosensors, graphene bactericide, deaf mute communication, scanners etc.

(c) Graphene uses and applications in electronics

Transistors, waterproof and wearable electronics, flexible touchscreens, hard drives, elastic robots, optoelectronics, superconductor.

(d) Graphene in structural application

Graphene in cement, silk, automobile, airplanes, ballistics, military equipment etc.

(e) Graphene applications in lubricants and coating application

Machinery lubricants, anticorrosive coatings, paints, radiation shielding, thermal and infrared vision etc.

(f) Graphene applications in food industry

Food packaging, water purification, desalination, crop protection, food security, etc.

In recent years, notable advancements in food processing have been made by integrating nanotechnology into food packaging systems. The inclusion of graphene-based nanomaterials in packaging materials has greatly improved their efficiency and functionality of packaging material [32, 33]. It plays an important role in the development of improved food packaging solutions with enhance mechanical properties, increase resistance to heat, improved barriers against oxygen, moisture, UV-rays, carbon dioxide, and volatile compounds and improved antimicrobial properties [34].

1.5 Introduction to packaging

Packaging refers to the science, art, and technique of enclosing or protecting products for the purposes of distribution, storage, sale, and usage. It serves to keep products safe and marketable while aiding in their identification, labelling, and shelf-life [35]. As such, it is a crucial sales tool that encourages consumers to make purchases. However, as human life transitioned from a nomadic lifestyle to settled living, the need for containers to store food became apparent. Until the 1800s, packaging materials were quite basic, primarily consisting of naturally occurring items like gourds, shells, and leaves with early packaging methods included weaving baskets from grass, wood, and bamboo. Eventually, materials like paper, glass, and pottery began to be used for carrying and storing food. Later, the introduction of corrugated boxes revolutionized shipping and transportation processes. In the 1890s, the National Biscuits Company was among the first to sell biscuits packaged in paper. However, using paper alone did not guarantee the quality of food upon reaching consumers. Glass bottles were commonly used but had significant drawbacks due to their fragility, thus, it was gradually replaced by metal cans that provided better protection against moisture and gases [36].

Following World War II, there was a heightened focus on improving food quality and safety, where the emergence of plastics in packaging, with polyethylene becoming one of the most widely used materials for food products. Although other plastics like polyethylene naphthalate (PEN) were approved by Food and Drug Administration for food packaging in 2000, their high cost limited widespread adoption [37]. Currently, over 40% of all plastics produced are utilized for packaging purposes, with nearly half designated for food packaging in forms of membranes/films, bottles, trays, sheets, tubs, and cups with most food wrapping materials that are derived from petroleum-based plastics [38]. However, these materials contribute to environmental pollution and landfill issues due to their chemical properties and slow degradation rates. Plastic packaging poses both ecological and health risks. Improper disposal leads to accumulation in landfills where it takes years to decompose while releasing microplastics and toxic gases during degradation. This presents a significant environmental challenge associated with plastic packaging materials shown in Figure 1.3.

Figure 1.3 Environmental challenges associated with plastic materials [35]

Plastic-based products are known for their high chemical stability and near-complete non-biodegradability under natural conditions. However, as illustrated in Figure 1.3, they can gradually break down into smaller particles through biological processes (involving bacteria, fungi, and algae), physical processes (including photodegradation, thermal degradation, and mechanical abrasion), and chemical processes (such as hydrolysis and thermal oxidation) [39]. This degradation produces tiny fragments less than 5 mm in size, referred to as microplastics (MPs), and those below 1 µm, classified as nanoplastics (NPs) [40]. MPs are generally divided into two main types according to their origin primary MPs and secondary MPs. Primary MPs can be designated as plastic particles deliberately designed and manufactured for several industrial applications to meet consumers demands while secondary MPs are formed from the breakdown of larger plastic items over time. According to a review article, MPs have been detected in diverse environments including deep and surface oceans, lakes, estuaries, shorelines, intertidal zones, mangroves, beaches, and sediments [41]. It was estimated that between 93,000 and 236,000 tonnes of MPs, equivalent to about 51 trillion particles, are currently floating on the ocean surface. It is estimated that over 80% of MPs originate on land, with less than 20% coming from marine sources [42]. Due to their lightweight, persistent, and buoyant nature, MPs can travel vast distances globally and their removal is extremely challenging. Even modern wastewater treatment systems cannot completely filter them out allowing these particles to enter rivers, oceans, and freshwater supplies [43]. Prolonged exposure to MPs significantly increases the risk of human contact with harmful chemical and additives. These tiny plastic particles, originating from various sources such as food packaging, medical devices, tire and rubber combustion, airborne dust, cosmetics, and common household items which may release toxic substances upon degradation [44]. Continuous interaction with these materials can lead to the accumulation of MPs in the human body, potentially causing adverse health effects. Exposure to MPs can occur through ingestion, inhalation, and dermal contact, leading to their accumulation in various human tissues. MPs frequently carry chemical additives (e.g., phthalates, BPA) or adsorb environmental pollutants like heavy metals and persistent organic pollutants (POPs) from their surroundings [45]. These chemicals may leach into the body, potentially disrupting the endocrine system and contributing to reproductive, neurological, and immune disorders, as well as increasing cancer risks [46]. To address these challenges, numerous industries and research groups are developing packaging solutions that are biodegradable, compostable, or easily recyclable. There is increasing emphasis on sustainable materials such as bio-based plastics, paper, cardboard, and plant-derived fibres. Contemporary packaging design also prioritizes recyclability, often by employing single-material formats or components that can be easily separated to facilitate sorting and recovery.

Biopolymers derived from renewable sources represent a significant advancement in food packaging towards a more sustainable society but exhibit shortcomings, particularly in terms of barrier properties, highlighting the need for research in new food packaging technologies and solutions [34]. In this context, polymer nanocomposites developed by combining different nanomaterials with unique characteristics, offers a promising path toward innovative high-tech packaging solutions. It has the potential to enhance various characteristics, including mechanical strength, thermal stability, barrier performance, cytotoxicity, microbiological resistance, and biodegradability.

Given the crucial importance of polymer-based packaging in contemporary society, the following sections is discussed with the most commonly used non-renewable and renewable polymers in food packaging industries.

1.5.1 Biopolymer

Biopolymers, also referred to as bioplastics, are derived from biomass or synthesized from monomeric units prepared using biomass. In recent times, there has been growing interest in bio-based materials and their cutting edge uses, especially in the realm of food packaging. Plastic materials sourced from petroleum are commonly utilized for food wrapping. However, their chemical and physical properties have led to environmental pollution and contribute to the depletion of landfill space, primarily due to their slow degradation rates. These challenges have prompted researchers to explore bio-based polymer films as a potential alternative to address the environmental concerns associated with plastic packaging waste [47]. However, biopolymers have demonstrated limited barrier properties and mechanical strength, often becoming brittle at low temperatures under heat distortion. Certain attributes are necessary for biopolymers to function effectively as packaging materials. The manufacturing of biodegradable polymers involves additional processes that maintain the material's biodegradability. These processes can be classified as synthetic (chemical) or biotechnological (utilizing enzymes or microorganisms). The primary methods include:

- **Polysaccharides and proteins**: Polymers derived from animal or plant-based polysaccharides (e.g., cellulose, starch, chitosan, alginate, carrageenan) or proteins (e.g., whey, soy, collagen, casein, corn zein, wheat gluten, gelatin, etc) [48].
- **Chemical synthesis from renewable resources**: Polymers chemically produced from monomers, which are obtained through biotechnological modification of renewable resources e.g., PLA, PVA, poly(ε-caprolactone) (PCL), poly (glycolic

acid) (PGA), poly (butylene succinate) (PBS) etc [49].

- **Biotechnological production from natural sources**: Polymers created through fermentation processes using natural microorganisms (e.g., thermoplastic aliphatic polyesters like poly(hydroxyalkanoates) (PHAs), including poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) and poly(β-hydroxybutyrate) (PHB), as well as microbial polysaccharides like pullulan and curdlan) [49].

The first category of biopolymers, derived from agro-based sources, is termed "agro-polymers," while the others are classified as biodegradable polyesters. Materials derived from renewable sources are often called "green" polymers. Biopolymers hold great promise for the development of commercially viable technologies and environmentally friendly solutions, offering a potential means to address sustainability challenges. A basic introduction to some biopolymers and additives used for the thesis work is described below.

1.5.1.1 Polyvinyl alcohol

Polyvinyl alcohol (PVA) is the most widely used synthetic resin globally and is classified as a water-soluble polyhydroxy polymer. PVA appears as a granular powder that is odourless, transparent or cream-colored. It is soluble in water, slightly soluble in ethanol, and insoluble in most other organic solvents. The melting point of PVA ranges from 180 °C to 190 °C, with a molecular weight between 26,300 g/mol and 30,000 g/mol and a hydrolysis degree of 86.5% to 89% [35]. PVA is one of the few linear aliphatic polymers that is not halogenated. Its structure features a two-dimensional hydrogen-bonded network sheet arrangement. PVA is produced by polymerizing vinyl acetate, which is then hydrolyzed to form PVA. The hydroxyl (-OH) groups present in PVA enables the formation of intermolecular interactions like hydrogen bonding, which play a key role in giving it a relatively high melting point of approximately from 200 °C. The polymer typically exhibits a zigzag structure and has semi-crystalline characteristics. PVA is highly regarded for its water solubility, biocompatibility, and low toxicity. Although it is hydrophilic, it still offers excellent gas barrier and strong tear resistance properties. Thus, to enhance its applicability of PVA in food packaging, crosslinking agents are often added to enhance in physiochemical properties, making it a popular choice in packaging industries for fruits and vegetable packaging [50].

1.5.1.2 Carboxymethyl cellulose

Carboxymethyl cellulose (CMC) is a water-soluble, anionic derivative of cellulose, a linear polysaccharide made up of anhydro-glucose units connected by β-1,4-glycosidic bonds. The primary distinction between CMC and cellulose lies in the presence of anionic carboxymethyl groups (–CH_2COOH) in CMC, which replace some hydrogen atoms from the hydroxyl groups of the original cellulose structure. The ease and low cost of synthesizing CMC, along with the availability of raw materials and its unique surface properties, mechanical strength, formability, tunable hydrophilicity, viscosity, and rheological characteristics, have led to its widespread use in various industries [51, 52]. These include biomedical, pharmaceutical, textile, construction, food, plastics, cosmetics, paper, and oil sectors. In biomedical applications, CMC and its composites are extensively utilized for tissue engineering, bone tissue engineering, wound dressings, absorbent nonwovens, fabrication of 3D scaffolds for biocompatible implants, and even artificial organs or mimics of extracellular polymeric materials.

1.5.2 Additives used in biopolymer-based composites in packaging

(a) Crosslinking agents

In chemistry and biology, a cross-link refers to a bond that connects one polymer chain to another. Crosslinking agents can be classified in various ways, primarily based on the type of bond formed, which includes covalent crosslinking, ionic bonds, physical interactions, hydrogen bonds, and Van der Waals forces. Another classification divides crosslinkers into three main categories: physical, chemical, and enzymatic [53]. The use of crosslinkers can enhance the mechanical and barrier properties of biopolymers, making them more suitable for food packaging compared to petroleum-based alternatives. By incorporating crosslinking agents, it is possible to create biopolymers that are resistant to heat and light while also reducing their water solubility and swelling tendencies. A diverse range of crosslinking agents is utilized in standard methods, including glutaraldehyde, epichlorohydrin, sodium tri metaphosphate, sodium benzoate, phosphoryl chloride, calcium chloride, citric acid, and boric acid [54].

(b) Plasticizers

Plasticizers are additives utilized to improve the durability, resilience, and ductility of polymers while simultaneously decreasing their stiffness and hardness. They function by reducing the strength and quantity of intermolecular forces within the material [55]. Typically, plasticizers are low molecular weight liquids that are particularly effective in polymers that are rigid at room temperature, as they lower the glass transition temperature.

This property allows films made from polymers to exhibit the necessary ductility and flexibility for various applications, such as plastic wrap. Common examples of plasticizers include Bis(n-butyl) phthalate (DBP) and Bis(2-ethylhexyl) phthalate (DEHP), both of which are frequently used in plastic wraps, with glycerol being one of the most widely used plasticizers overall [56, 57].

1.5.3 Graphene-based polymer nanocomposite packaging films

Over the years, particularly in the last century, food packaging strategies have evolved significantly, with materials chemistry playing a vital role in developing innovative packaging solutions. The combination of traditional polymers with various materials has led to the emergence of new composite materials that exhibit enhanced properties. Notably, nanomaterials such as graphene (Gr), GO, and rGO have been integrated into composites with polymers like PLA, starch (ST), polystyrene (PS), polyhydroxybutanoate (PHB), cellulose, polyethylene terephthalate (PET), chitosan (CS), polypropylene (PP), PVA, etc [58,59]. The interactions of Gr and its derivatives with these polymers take place via chemical bonds or molecular forces, leading to enhancements in their mechanical, chemical, thermal, antimicrobial, and barrier characteristics. Gr-based NCs have shown promise in enhancing UV resistance and acting as effective barriers against gases while maintaining superior physiochemical, electrical properties compared to their polymeric matrix [60,61]. Gr-based nanomaterials combined with biodegradable polymers act as antimicrobial and antioxidant agents in active packaging, enhancing food quality, safety, and shelf life. In smart packaging, Gr can also serve as a sensor to detect biochemical or microbial changes, monitoring pathogens, gases, oxygen levels, and spoilage to ensure food safety and quality. Among different graphene derivatives, GO is especially promising for packaging applications because of its exceptional properties, such as superior barrier performance, strong mechanical strength, excellent thermal and electrical properties, large surface area, high carrier mobility, and antibacterial and antifungal properties [34].

Graphene oxide consists of a single graphene layer decorated with various functional groups. The individual sheets of graphite oxide can be isolated through exfoliation. Several exfoliation techniques have been reported, including high-temperature treatment, microwave irradiation, focused solar energy, laser processing, solvothermal methods, ultrasonication, and solvent-assisted exfoliation, for producing graphene oxide [20].

Although, GO offers significant advantages, its adoption must also be considered in the context of environmental impact, particularly in comparison to conventional petroleum-based plastics. Petroleum-based polymers pose significant environmental challenges as they are non-biodegradable, leading to long-term accumulation in landfills and marine ecosystems [38]. Their production depends heavily on fossil fuels, resulting in resource depletion and substantial greenhouse gas emissions. Moreover, during degradation, they often release microplastics and toxic additives that threaten both ecosystems and human health [46]. In contrast, GO derived from naturally abundant graphite, has emerged as a promising alternative. Owing to its surface functional groups and unique two-dimensional structure, GO can significantly improve the mechanical strength, thermal stability, and barrier properties of polymer matrices [20]. When incorporated into biodegradable polymers, it reduces overall material use, extends product lifespan, and supports the creation of high-performance composites with lower environmental burdens. Despite these advantages, the release of GO during its life cycle may lead to nanoparticle accumulation in the environment, posing risks such as oxidative stress, inflammation, and toxicity [62]. In conclusion, petroleum-based polymers present significant environmental challenges due to their persistence, fossil fuel dependence, and microplastic pollution. While, GO offers notable improvements in material performance and sustainability but poses potential risks from nanoparticle release. Therefore, its responsible adoption requires thorough life-cycle assessments, safe handling practices, and the development of green synthesis methods and regulatory frameworks to ensure environmental safety.

1.5.4 Methods for fabricating filler/polymer nanocomposites

Nanocomposites, consisting of a polymer matrix integrated with nanoparticles, can be produced through several techniques. These fabrication methods are generally classified into following categories: solution intercalation, in situ polymerization, sol-gel processes, and direct mechanical mixing which are discussed below [63,64].

(a) In-situ polymerization

This general method outlines the synthesis of polymer nanocomposites through the mixing of monomers and nanoparticles in a suitable solvent. Essentially, nanoparticles are intercalated with the monomers, followed by polymerization using an appropriate reagent or free radical initiator, resulting in the formation of polymer nanocomposites. The resulting products offer numerous advantages, including thermodynamic stability and improved material properties due to better dispersion of the nanofillers. This approach is based on the bottom-up methodology and allows for the creation of multidimensional structures with properties that differ significantly from those of the original precursors [63].

(b) Solution intercalation

The solution intercalation method is one of the simplest traditional approaches for fabricating polymer films with varying thicknesses [64]. It is widely used on a laboratory scale to prepare polymer nanocomposites due to its versatility, allowing the use of various solvents in a straightforward and efficient process. In this method, polymer is dissolved in a suitable solvent, and the components are mixed using techniques such as simple stirring, shear mixing, or ultrasonication to disperse nanofiller within the polymer matrix. Ensuring complete solvent removal and achieving uniform dispersion are critical steps in NC production, as residual solvent can negatively impact the material's properties by acting as a plasticizer or remaining on the surface. In the solvent evaporation process, improving solubility in the selected solvent is crucial to avoid nanoparticle agglomeration. However, this method has drawbacks, such as the limited solubility of certain polymers in common solvents and the need of large amounts of solvent.

(c) Melt intercalation

The melting method is a process well-suited for industrial applications, particularly for producing thermoplastic-based NCs, due to its fast and cost-effective nature [63]. In this method, polymer disentanglement occurs in the molten state, allowing the polymer chains to move freely and mix thoroughly. NCs prepared through melt mixing generally demonstrate good filler dispersion. However, careful control of the mixing temperature is essential to prevent polymer degradation at elevated temperatures. Additionally, the process requires high shear forces for effective mixing, which lead to the formation of wrinkles, or even breakage of nanoplatelets, thus reducing the effective modulus. Following melt mixing, further steps such as hot pressing and injection molding are required. The dispersion process allows for controlling the surface modification of nanofillers, ensuring compatibility with the polymer and optimizing processing conditions.

(d) Interfacial polymerization

The interfacial polymerisation approach comprises mixing the nanofiller, initiator, and monomer in two immiscible liquids. Before combining, the nanofillers are exfoliated with ultrasonic technology. The two immiscible liquids, representing the organic and aqueous phases, are then mixed. During the process, the reactants diffuse to the interface, where the monomer binds to the nanofiller. Polymerisation happens at the interface of two immiscible liquids, resulting in intercalation or exfoliation of polymer chains inside the nanofiller layers. In some cases, this approach necessitates the use of a solvent, followed by extra refinement processes to eliminate liquid. The method offers several advantages, including ease of implementation, scalability, cost-effectiveness, and minimal environmental impact.

(e) Electrospinning

Since late 1990s, electrospinning (electrostatic fiber spinning) has emerged as an advanced, modern, and adaptable technique, recognized for its simplicity in producing nanofibers from various materials [65]. The fundamental principle of electrospinning involves spraying a solution, suspension, or melt in a strong electric field to fabricate microscopic threads with diameters that can be as small as nanometers. The electrospinning technique is capable of producing nanofibers from a wide variety of polymer types, including natural polymers such as chitosan, cellulose derivatives, collagen, silk, alginate, and gelatin, as well as synthetic polymers like tyrosine-derived polycarbonates, PVA, PLA, PGA, PLGA, and poly (vinyl pyrrolidone) etc along with their blends. Electrospun nanofibers have extensive applications across various fields, including composites, tissue engineering, biomaterials, food packaging, sensors, energy storage and conversion, flexible electronics, drug delivery and release, catalysts, etc.

1.6 Polymer nanocomposites characterization techniques

Various characterization techniques are available to assess the performance of nanocomposites, as discussed below.

(i) Morphology analysis

(a) Scanning electron microscopy

Scanning electron microscopy (SEM) is a highly effective analytical method used to examine various materials at high magnifications, yielding high-resolution images. This technique is extensively employed to characterize the morphology of a material.

(b) Transmission electron microscopy

Transmission electron microscopy **(**TEM) is a sophisticated analytical technique utilized to observe the smallest structures within materials. Unlike optical microscopes that depend on visible light, TEM provides extraordinary detail at the atomic level by magnifying nanometer-scale structures up to 50 million times. This capability allows for comprehensive micro-structural analysis through high-resolution and high-magnification imaging for investigating various biological and material samples, including tissues, cells, sub-cellular components, proteins, as well as crystalline and composite materials.

(ii) Physical property

(a) Conductivity

This is a measurement of a material's capacity to conduct electrical current. Electrical conductivity in composite materials is determined by the type and quantity of conductive fillers used or different type of conducting polymer used in the matrix.

(b) Viscosity

It is a characteristic of a fluid that hinders internal movement or, fluid resistance to flow.

(c) Contact angle

The surface properties of a membrane, such as hydrophilicity and hydrophobicity, can be evaluated using a contact angle analyzer. This technique measures the angle created between a liquid (typically water) and the solid surface of the membrane. By convention, surfaces with a water contact angle greater than 90° are classified as hydrophobic, while those with a contact angle below 90° are classified as hydrophilic.

(iii) Mechanical properties

(a) Tensile property

Tensile testing evaluates a material's capacity to endure tensile loads without failing and assesses its ability to deform under tensile stress. For polymers, these tests determine key properties such as tensile strength, tensile modulus, tensile strain, and elongation at yield or break. These characteristics are crucial for assessing whether a material is suitable for particular applications or likely to fail under specific stresses.

(b) Rheology

Rheology focuses on the study of matter's deformation and flow, offering a fundamental understanding of material behaviour. This involves analyzing both elastic behavior (where materials revert to their original shape once the stress is removed) and plastic behavior (where materials undergo permanent deformation).

(iv) Thermal behaviour

(a) Thermogravimetric Analysis

Thermogravimetric Analysis (TGA) assesses the weight variations of a material relative to temperature, offering valuable information about the thermal stability and degradation behavior of nanocomposite films.

(b) Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry **(**DSC) investigates thermal transitions such as melting and crystallization temperatures, which are essential for understanding the processing conditions and functional performance of nanocomposites.

(v) Barrier properties

(a) Water vapor permeability

The ability of material to facilitate the diffusion of water vapour through them is known as their water vapour permeability (WVP). This characteristic is crucial in a number of applications where moisture management is necessary, such as food packaging, textiles, and membranes.

(b) Moisture retention capacity

Moisture retention capacity **(**MRC) is the ability of a material is to hold and maintain moisture over time. This feature is especially relevant in industries like agriculture, construction, and packaging, where moisture levels have a substantial impact on performance and use.

(vi) Optical properties

Color characteristics and UV barrier properties (transparency and opacity) are essential features of food packaging materials. These properties not only allow consumers to observe the food products but also impact the overall acceptability of the items. Color measurements and UV-Vis property of polymer materials are evaluated by colorimeter or spectrophotometric instruments.

(vii) Chemical stability and physico-chemical interaction between phases

Fourier Transform Infrared Spectroscopy (FTIR) analysis has been performed to analyse the chemical stability and physico-chemical interaction between phases. It is an important method in chemistry and materials research for detecting chemical structures and studying material properties that interact with infrared light.

(viii) Antimicrobial activity

The antimicrobial characteristics of a film is its ability to prevent or inhibit the proliferation of microorganisms, including bacteria, fungi, and viruses, on its surface. Films engineered with antimicrobial properties are typically intended to avert microbial contamination, rendering them essential for uses where hygiene and safety are paramount, such as in food packaging, medical instruments, and wound dressings.

(ix) Biodegradation behaviour

Biodegradability testing evaluates a material's ability to break down into natural components like carbon dioxide, water, and biomass through the activity of microorganisms such as bacteria, fungi, or algae. This testing is crucial in determining whether a product is eco-friendly or poses environmental risks upon disposal. Different types of degradation analysis are stated below

(a) Soil Biodegradation

This method evaluates how materials decompose in soil. Given that many plastic films and similar products are designed for outdoor use, it is essential to confirm that they break down safely without compromising soil quality.

(b) Microbial degradation

The breakdown of polymers by microorganisms is known as microbial biodegradation. This process involves the attachment of microbes to the plastic surface, followed by their growth using the plastic as a source of carbon.

1.7 Motivation and research objectives

The increasing need of eco-friendly, high-performing packaging solutions has spurred innovation to address the shortcomings of traditional polymer-based materials. Although biodegradable synthetic polymers such as PVA possess desirable characteristics like superior film formation, but faces limitations in mechanical, and barrier properties. These limitations hinder their widespread adoption in cutting-edge packaging applications.

Thus, to address these limitations, the present thesis is motivated by the potential of nanotechnology and biopolymer blending as promising strategies to enhance the functional performance of polymer-based materials. Specifically, the incorporation of GO as a nanofiller is envisioned to significantly reinforce the polymer matrix, leading to improved mechanical, thermal, barrier, and antimicrobial properties. Furthermore, blending PVA with natural biopolymers CMC is expected to not only enhance material characteristics but also contribute to sustainability through the use of renewable, biodegradable, and environmentally friendly components.

The motivation further extends to explore the potential of electrospinning fabrication technique to develop novel PVA/CMC/GO nanofiber mats with improved structural stability and functional capabilities. The technique enables precise control over structural and morphological properties, which is crucial for achieving optimal performance of nanofiber mats in both packaging and biomedical applications.

Ultimately, the research aspires to contribute multifunctional hybrid materials with improved durability, functionality, and environmental sustainability by systematically examining the impact of GO nanofiller concentration, CMC incorporation, and electrospinning conditions. Thus, the overarching goal is to provide a sustainable alternative to conventional plastic packaging materials, thereby reducing environmental harm and fostering innovation in the domain of bio-based nanocomposites.

1.8 Thesis Outline

The thesis consists of six chapters, and a brief summary of each chapter is provided below.

Chapter 1

This chapter covers the comprehensive introduction of the research work.

Chapter 2

This chapter compiles relevant literature that serves as a guiding light for the thesis.

Chapter 3

This chapter covers the materials and methodology used for fabrication and characterization.

Chapter 4

This chapter highlights the development, characterization and potential perspective of poly (vinyl alcohol)/graphene oxide nanocomposite films.

Chapter 5

This chapter highlights the development and characterization of biodegradable poly(vinyl alcohol)/carboxymethyl cellulose composite films.

Chapter 6

This chapter highlights the synergistic effect of graphene oxide on the properties of poly (vinyl alcohol)/carboxymethyl cellulose electrospun nanofiber mats.

Chapter 7

This chapter serves as the concluding section of the thesis, summarizing the overall work, highlighting the key findings, and discussing potential future directions for the study.

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