Chapter

Bioinspired Nanocomposites: Functional Materials for Sustainable Greener Technologies

Sarmad Ahmad Qamar, Muhammad Asgher and Nimrah Khalid

Abstract

This chapter presents a broad overview of the current advancements in bioplastics and bioinspired nanocomposites with nanoscale reinforcements that are being applied for a broad range of applications, that is, biomedical, electronics, durable goods and packaging materials. The production of nanocomposites by completely and/or partially renewable and biodegradable materials has helped in a range of different applications. Several drawbacks of conventional materials such as hydrophilicity, low-heat deflection, poor conductivity, and barrier properties can be efficiently overcome using biohybrid nanomaterials. *Nano*-reinforcements in composite materials deliver remarkably improved properties such as decrease in hydrophilicity and increase in mechanical properties as compared with neat biopolymer, which fails to exhibit these properties on its own. This approach can be used for other natural polymers to induce desired functionalities. This chapter covers the recent trends in nano-functional materials, renewable materials that are being applied for the production of nanobiocomposites and their applications especially in biomedical and healthcare sectors, which are discussed in detail. This emerging concept will definitely enhance the scope of nanohybrid materials for sustainable products development with improved properties than previously applied synthetic polymer-based or natural polymer-based materials.

Keywords: bioplastics, nanobiocomposites, multifunctional materials, biomedical applications

1. Introduction

Synthetic polymers are widely being used in everyday life for various applications. They can meet industrial and commercial market requirements, for example, durability, convenience, good performance, low cost, and high variability in regard to mechanical and barrier properties [1]. A significant amount of plastics is being used for packaging applications, which has grown rapidly from previous two decades [2]. These synthetic polymers/plastics of petrochemical origin are highly resistant to biodegradation, causing serious threat to the environmental sustainability because of the accumulation of nonbiodegradable wastes, which is increasing every year. Overdependence of fossil resources can be reduced by the development of bio-based materials using renewable resources. Currently, bioplastic market is progressing with an annual growth rate of 30% of synthetic plastic market [3]. Many scientists are working on the production of new compounds of biological origin either by chemical modifications or by industrial biotechnological processing. Efforts are being made for the production of biopolymers or polymer building blocks using microorganisms and/or plants such as exopolysaccharides and other polyesters [4]. For the betterment of material characteristics, different types of polymers are blended together, which is known as composite material, and the materials with nanoscale reinforcement (i.e., at least one nanoscale dimension) are called nanocomposite materials.

Polyhydroxyalkanoates (PHA) production has significantly progressed; recently it has been demonstrated that the lignocellulosic components of residual of sugarcane bagasse are effective fermentation biomaterials for PHA production. The concept of utilization of waste-based biomass is promoting sustainable, bio-based economy [5]. Bio-based and/or biodegradable plastics may include some biopolymers derived from and/or returned to the nature. The terms "biodegradable" and "bio-based" are used interchangeably, but it is not correct. Bioplastics can be manufactured from biodegradable petro-based polymers, renewable materials, or some combination of these. The various types of plastics available in the market are presented in **Figure 1**.

The development of novel nanohybrid materials for the induction of desired characteristics among polymer matrix is an emerging area among life sciences, material sciences, and nanotechnology. During the previous decade, "nanobiotechnology" became a familiar term, used to indicate nanohybrid materials involving natural-based or a biopolymer conjugated with inorganic moieties [6]. Since the development of nanocomposite materials, huge efforts were made by the scientists because of outstanding characteristics of these nanohybrid materials for both functional or structural materials, comprising amazing applications as electrochemical devices, and heterogeneous catalysts [7].

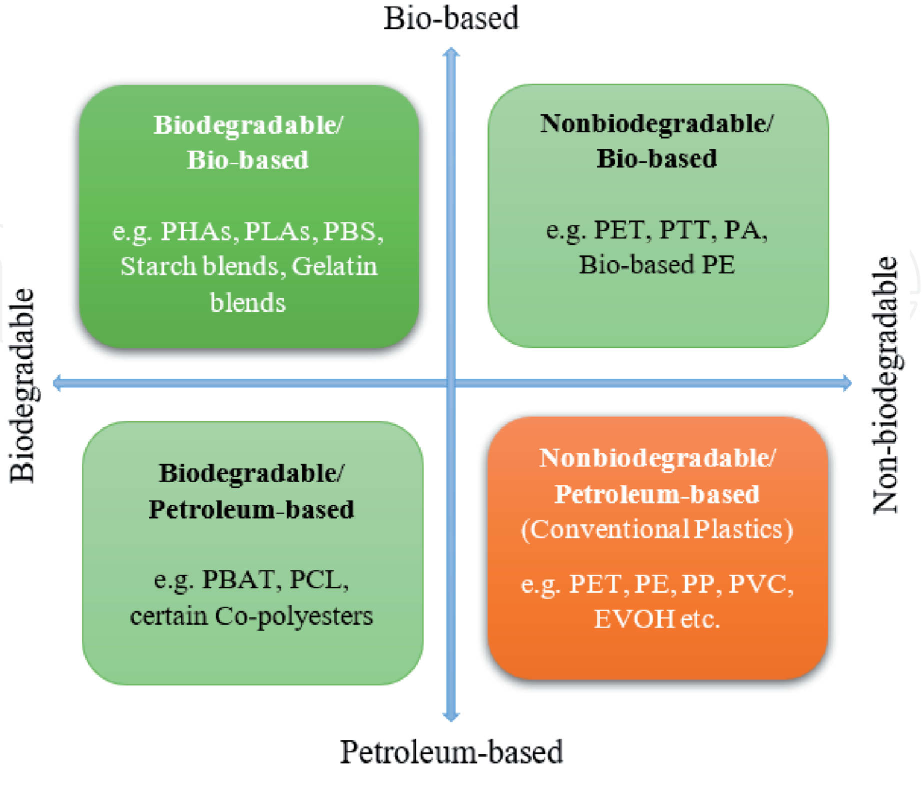

Figure 1.
Various types of plastics available in the market from origin and degradability point of view.

Researchers in nanotechnology are now focusing on the development of biopolymer-based nanocomposites that present outstanding characteristics similar to synthetic polymer-based materials (i.e., better thermal stability with improved mechanical and barrier properties) [8, 9]. In addition to these properties, nanobiocomposites also present remarkable advantage of biodegradability, biocompatibility, and, sometimes, functional characteristics provided by inorganic or biological moieties. The increasing interest in nanobiocomposites can also be imagined by the number of publications in previous two decades as per Web of Science, ISI database (**Figure 2**).

Several research groups are making efforts to replace petroleum-based polymers by natural, biodegradable, and abundant products synthesized from renewable biomass [10, 11]. Various biomacromolecules are present in nature, which could be utilized as renewable biomass for the production of nanohybrid materials such as starch, cellulose, lignin, polylactic acid (PLA), and other polyesters for the development of "greener" materials [12, 13]. Their blends with natural inorganic materials, for example, nanocellulosic-clay and carboxymethylcellulose, provide enhanced biodegradability and biocompatibility among matrix molecules.

Microbes are able to decompose biologically originated molecules, giving CO_2, which is utilized by the plants during the process of photosynthesis. The applications of these bio-based nanohybrid materials in the agricultural, biomedical, and/or in other areas will definitely help in the maintenance of environmental sustainability. Biomacromolecules or biopolymers bearing functional moieties representing highly specific catalytic properties, for example enzymes, present significant role in the production of nanobiocomposites aiming to produce nanohybrid materials with required characteristics. In nanobiocomposites that are based on enzymes, the inorganic portion is considered as the protective matrix for the immobilization of macromolecules and imparts multifunctionality to the nanohybrid matrix [14, 15]. The production of inorganic hybrid enzymes is an alternative way toward enzyme immobilization, which is a useful method for the development of enzymatic reactors and biosensors.

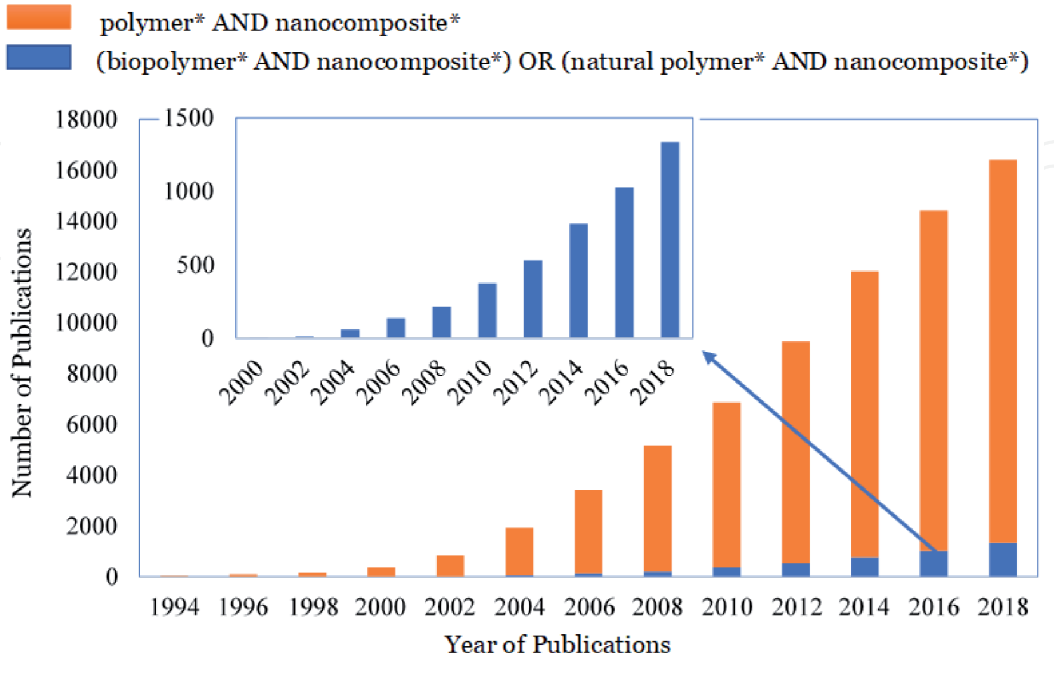

Figure 2.
Graphical representation of year-wise number of scientific publications related to synthetic polymer composites and bio-based nanocomposites (Web of Science, ISI statistics).

2. Nanocomposites from renewable resources

Currently, a growing concern among industrialists and researchers is to use environmentally friendly substances, aiming to replace nondegradable substances, thereby reducing the long-term accumulation of plastic waste in the environment. Biocompatible and biodegradable materials having applications in agricultural, food, or healthcare sectors are the major goals of several scientific studies. Petroleum-based materials are being replaced by natural/biological and/or biodegradable materials, which are also renewable in natural environment; for example, cellulose, starch, polycaprolactone, and PLA are being used to synthesize biodegradable packaging materials [16, 17]. These renewable materials consist of nontoxic compounds that are capable of biological degradation by several soil microorganisms. This emerging concept will definitely help in the reduction in environmental damage due to petrochemical dependence.

Because of huge benefits of renewable materials with environmentally sustainable nature and a broad spectrum of various industrial and healthcare applications, several scientific studies are focusing on the development of bio-based materials with improved characteristics [18, 19]. This has led toward the production of biodegradable nanocomposites that can exhibit more improved properties than nonreinforced bioplastics. Biomacromolecules, for example cellulose, starch, and their derivatives, are natural polymers used for the production of nanobiocomposites [20, 21]. These materials include synthetic or natural clay minerals or modified clay minerals such as nanofiller, providing exfoliation or intercalation compounds. Cloisite and montmorillonite are commonly applied silicates in these researches, having function of nanocharges that can act as reinforcement in the biopolymer material, resulting in improved mechanical strength of biopolymeric films.

Plasticizers are the substances added to synthetic resins to increase flexibility and plasticity to make the resulting plastic less brittle. Typically, glycerol, vegetable oil, or tryethylcitrate are added as plasticizers to bioplastic films with melting temperature near decomposition to prevent them from degradation, resulting in good-quality thermoplastic polymers. Plasticizers also contribute to better nanofiller dispersion in the matrix, giving amazing mechanical properties. Thermoplastic PLA, produced by cornstarch fermentation, is a most frequently used biopolymer for the production of bioplastic blended with organically altered silicates [22, 23]. The addition of titanate as a nanofiller to PLA bioplastics results in improvement in biodegradation, comparable to TiO_2 [24].

Although various researches comprising recent available data on nanobiocomposites have been explained above, the production of nanobased biocomposites is still in the developing phase. Further progress lies in the development of new materials by using novel biopolymers, to increase their compatibility with inorganic moieties. Polysaccharides and other natural macromolecules, and their integration with several nanofillers other than silicates and silica, for example, LDHs, would help in the improvement of mechanical and barrier properties of nanobiocomposites. Besides the improvement in mechanical properties, clay films also exhibit improved gas barrier and thermal stability that can be used for food packaging applications [25, 26].

Nanocomposites that comprise synthetic polymers and inorganic reinforcements, the distribution of silicates in biopolymer matrix initiates the "tortuous" pathway, leading to reduction in gas diffusion property of nanohybrid materials. In addition to silicates, several different inorganic solids have been added as reinforcements to biopolymer materials; for example, the distribution of sepiolite in natural rubber causes improvement in mechanical properties [27]. Tensile strength and elastic modulus of natural rubber are increased by the addition of single walled carbon nanotubes (SWCNTs) and SiC nanoparticles-based reinforcements, have become improved that those with just SWCNTs-based materials [28]. Multiwalled carbon nanotubes (MWCNTs) dispersion in natural rubber materials also represented a similar effect, for example, improved physical, mechanical, and chemical properties of biopolymer [29, 30] as presented in **Figure 3**.

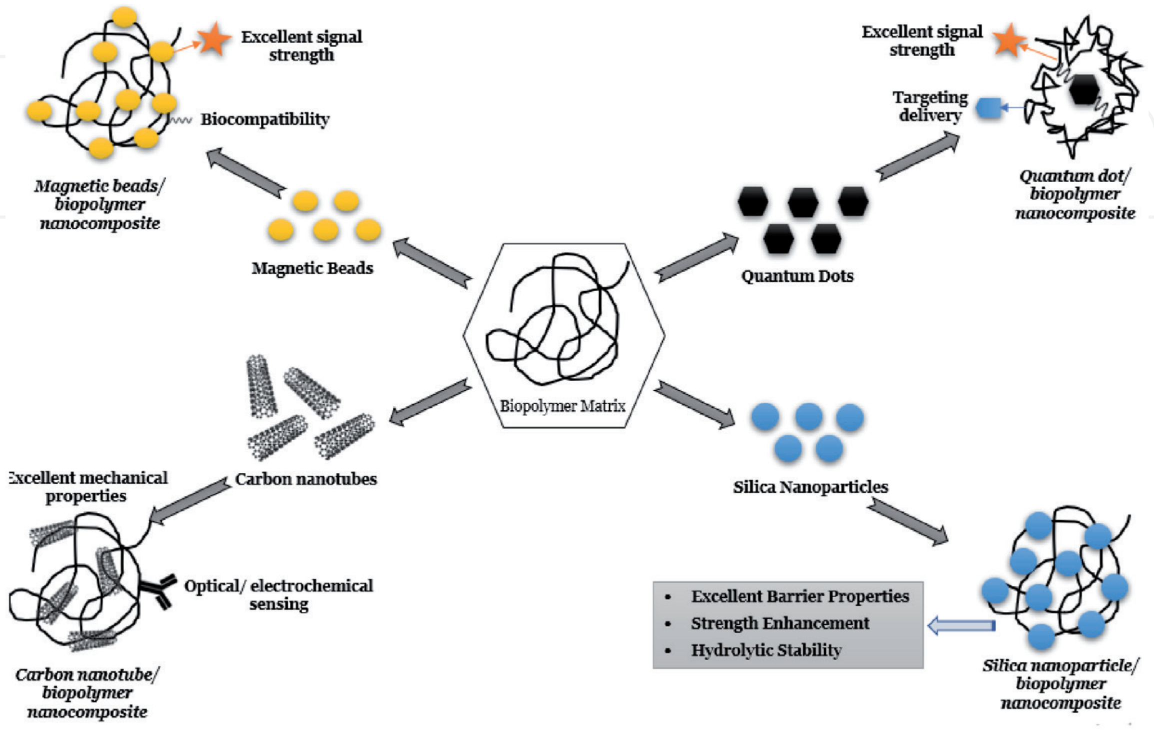

Figure 3.
Different types of nanostructured reinforcements among biopolymer matrix to induce desired functionality.

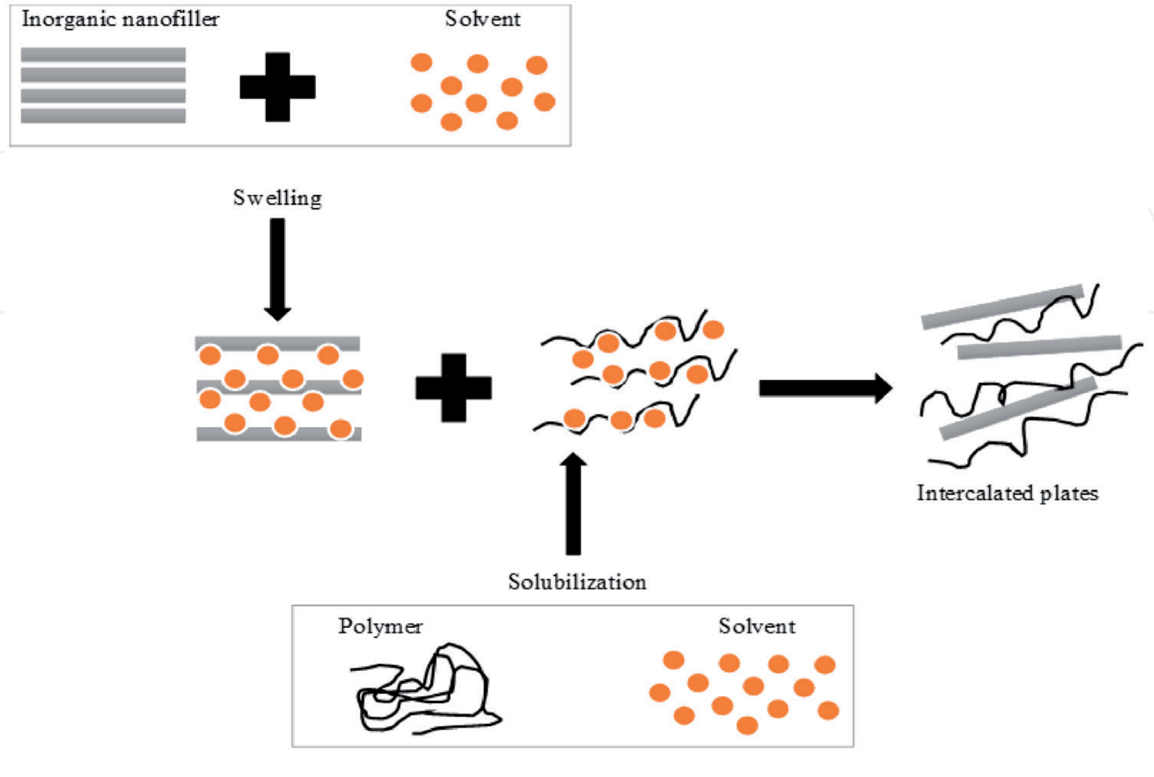

Figure 4.
Crosslinking between inorganic nanofiller and polymer matrix to form intercalated plates with improved tensile strength and modulus.

Organic reinforcement of starch and cellulose whiskers has become a sustainable replacement to other inorganic fillers; for example, nanocrystals of maize starch have been utilized as nano-reinforcement in glycerol plasticized maize starch [31, 32] leading toward improvement in mechanical properties of nanocomposites (**Figure 3**). Improvement in mechanical characteristics was also observed by the use of sodium carboxymethyl cellulose whiskers synthesized from cotton linter pulp when employed as reinforcement [33]. Enhancement in both Young's modulus and the tensile strength was observed, caused by the nanofiller and polymer matrix crosslinking resulting from intermolecular hydrogen bonding as shown in **Figure 4**.

The interest in using environmentally friendly, that is, biodegradable, products is increasing among companies; for example, NEC and Fujitsu have started to commercialize environmentally friendly mobile phones and notebook computers based on PLA-chips, reinforced with kenaf fibers or petrochemically derived polymers. The electronic applications will require more researches on enhancement of characteristics regarding distribution of biodegradable whiskers in polymeric materials.

3. Development of nanocomposite materials

Development of nanohybrid materials is a stepwise approach such as breakdown of intermolecular bonds comprising less energy, shaping new orientation and arrangement, and the production of new 3D network of polymeric substance by new interaction and bonds. Formation of new intermolecular forces relies upon polymer shape (length/diameter, ratio) and also the conditions provided. The material formed is stabilized by electrostatic, hydrophobic, covalent, and hydrogen bonds. Dry and wet processing of polymers is frequently reported useful for the synthesis of biopolymer-based nanocomposites [34]. Dry processing depends upon the thermoplastic characteristics of polymer, in which mechanical and thermal treatments cause induction of disulfide/sulfhydryl exchange reactions, while wet process depends on solubilization, type of solvent used, and pH, which can alter the polymer conformation [35].

3.1 Wet processing

Wet processing, also referred to as continuous spreading or casting method, is commonly used for the manufacture of bio and nanocomposites from natural resources, such as carbohydrates, proteins, and lipids (**Figure 5A**). Wet processing is based on polymer solubilization in a suitable solvent for the production of film forming solution. Desired additives (filler, plasticizers, antioxidant, antimicrobial compounds, nano-/microparticles, cross-linking agents) are added in the resultant solution. The method is followed by film spreading and solvent evaporation. Plasticizer addition is useful as it decreases intermolecular attractions and stiffness by giving flexibility and smoothing handling. This method is useful for packaging material development and it improves the mechanical properties of the resulting material [36].

3.2 Dry processing

As described above, this process is based upon thermoplastic properties of polymers that have an outstanding role in the synthesis of composite material. It can be correlated with glass transition theory, in which a glassy material is changed into a viscous state at a specific temperature. Transition state basically induces disorder, mobility, and free volume by changing physicochemical as well as mechanical properties of a substance [37]. In general, polymers can be shaped into desired material

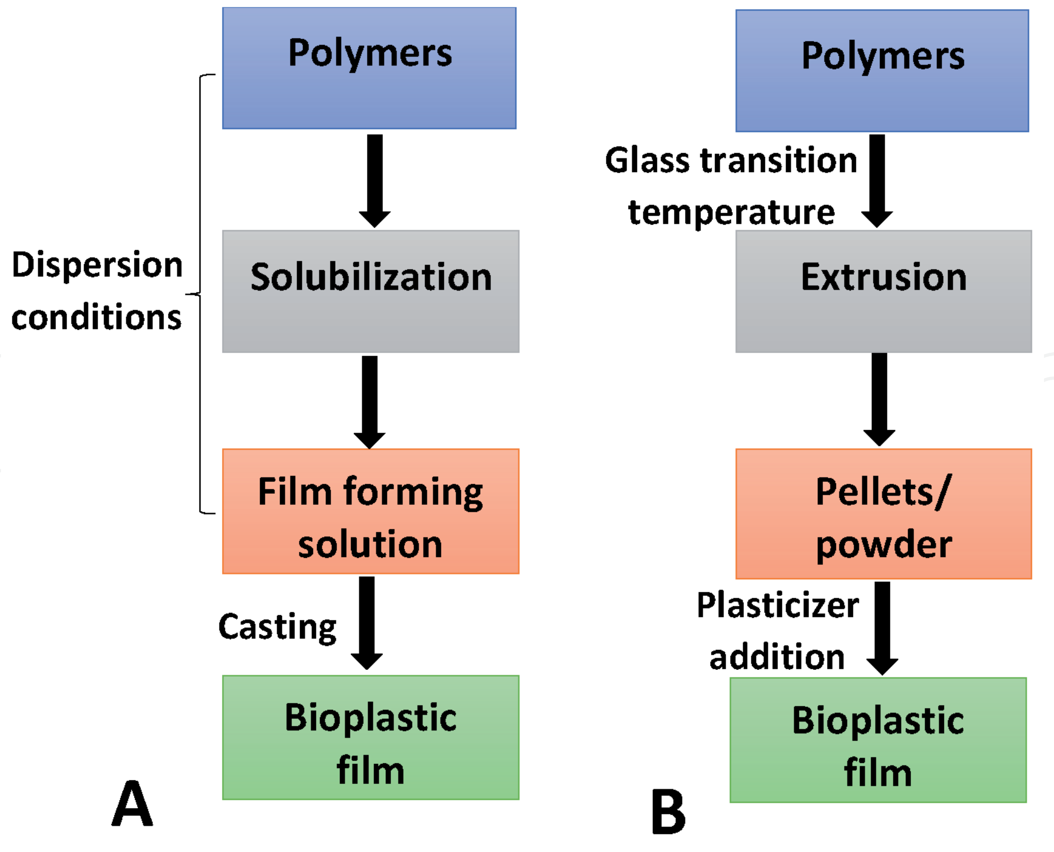

Figure 5.
Developmental strategies of bio/nanocomposites for functional applications: (A) wet processing; (B) dry processing.

by addition of plasticizer at high temperature and providing shearing force. Proteins denature at high temperature and the bonds in their molecules break, and new bonds and links establish in their molecules causing change in material properties [38]. Materials based on polymeric dry processing can be manufactured by several ways, for example, thermal processing or extrusion technique (**Figure 5B**). These processes can be used independently or both at the same time, in which extrusion is used for mixing and limited modification and thermal processing for the synthesis of final product.

4. Nanobiocomposites in healthcare sector

Nanobiocomposites present various applications especially in biomedical sciences like tissue engineering. The development of nanocomposites for regenerative medicine with bone implants and tissue engineering is still considered an emerging field [39, 40]. PLA and collagen are the most widely studied biopolymers for tissue regeneration as they provide artificial support for growth of the cells. This bioresorbable scaffold requires suitable mechanical properties and sufficient macroporosity with interconnected pores to avoid collapse of implantation and to allow the transportation of metabolic substances and the nutrients, and to control biodegradability [41]. Most of the articles published are related to bone repair. Thyroid hormones have important role in proper metabolism and functioning of the body such as cardiovascular homeostasis [42] and normal kidney function [43, 44]. Abnormalities in thyroid hormone production can cause serious health issues. Recent progress in the development of nanoscale biocomposites has led toward the development of catalase immobilized nanotubes *graft*-poly (L-lysine) for the diagnosis of iodate and H_2O_2 [45].

Nanobiocomposites tested and implanted for tissue regeneration include hydroxyapatite (HAp/collagen) to reproduce biocompatibility, composition, and mechanical properties of bones [46]. Other biopolymers, for example, chitosan [47], PLA [48], silk fibroin [49], and alginate [50] have also been studied in combination with HAp for the development of suitable bone regeneration scaffold. These implants mimic the surface roughness, porosity, and nanostructure of natural bones, as this facilitates the propagation of osteoblasts and helps in the regeneration of bones. Various synthetic techniques, for example, phase separation, gas foaming, fiber bonding, and freeze-drying/emulsification have been used to synthesize foam-like biocomposites with interconnected pores and suitable porosity [51, 52].

Future improvements in this area could be the replacement of HAp in natural polymers with some inorganic or the combination of organic/inorganic reinforcements. Sepiolite comprising microfibrous morphology has been blended with polymers, for example, collagen, giving rise to high-quality multifunctional hybrid materials [53]. High affinity between sepiolite and collagen biopolymer leads toward alignment with sepiolite fibers. Degradation rate can be reduced by the treatment of this biomaterial with a crosslinker, for example, glutaraldehyde, that increases mechanical properties, enhancing persistence after tissue implantation [54].

Nanobiocomposites also have a range of different applications, for example, drug delivery system [55] due to reduced dimensions and biocompatibility (**Figure 6**). Various studies have been reported in past few years about nanobiocomposites in targeted drug delivery system [55, 56]. The use of layered double hydroxide nanostructure (LDH) transporter as a non-viral vector for gene therapy has also been studied [57]. DNA intercalation in environment of Mg-Al/LDH by ion-exchange chromatography has also been confirmed. Analysis by XRD showed the increase of interlayer distance, revealing LDH parallel conformation to DNA double helical structure. The DNA transfer mechanism relies upon the shielding effect induced by the negative charge of DNA structure. This conformation facilitates the transportation of hybrid

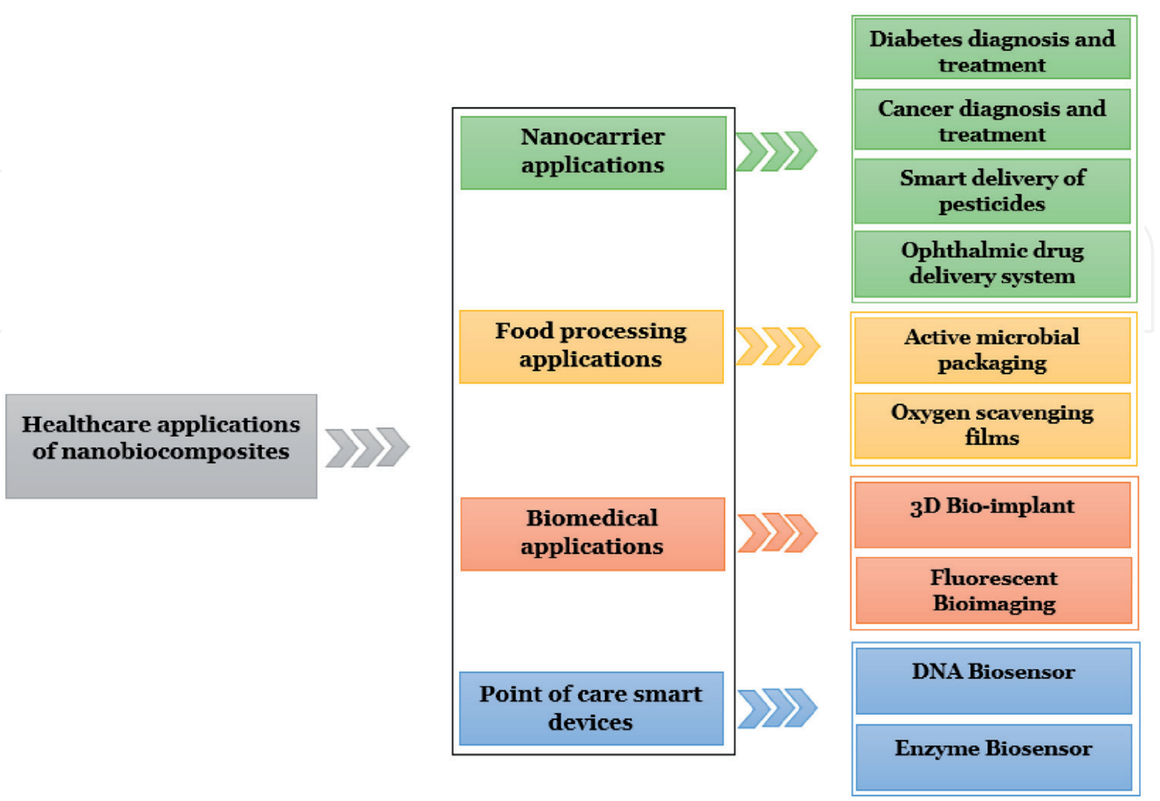

Figure 6.
Applications of nanobiocomposites in healthcare sector.

structure through the cell membrane, leading to LDH dissolution at acidic pH in lysosomes, the movement of DNA to the nucleus [58]. Nanosized hybrid materials, suitable for drug delivery purposes, have also been extensively studied for the treatment of leukemia and diabetes using gene therapy [59, 60].

5. Summary and future perspectives

There has been an explosion of scientific interest among nanotechnologists and material scientists to use biomass as a source of renewable materials and energy. For this purpose, the utilization of neat biopolymers comprises several limitations, that is, poor mechanical and barrier characteristics, which can be efficiently overcome using nanomaterials as reinforcing agents. The term "nanomaterials" covers a range of different materials with at least one dimension in nanoscale, that is, nanocrystals, nanoparticles, nanotubes, dendrimers, and several other inorganic nanoparticles. The use of "green chemistry" approach for the development of nano/biocomposite materials comprises several advantages over conventional materials processing strategies, that is, their environmentally friendly, biocompatible, and biodegradable nature. Biocompatibility is an important property for the application of these nanohybrid materials in healthcare sector including regenerative medicine, tissue engineering, or food industry.

Efforts are being made for the development of HAP-based nanocomposites for bone-engineering purposes. Another most important use of nanohybrid materials is targeted drug delivery, and the development of non-viral DNA vectors for gene therapy. Several functional nanohybrid materials working as optical and electronic gadgets are also being developed. Another promising application is the production of bio-based nanohybrid products, integrating natural-based polymers like chitosan, that have strong ion-exchange ability and effective electrochemical sensors. Enzyme entrapment by using several inorganic materials has led toward the production of active nanobiocomposites that can be efficiently used in bioreactor and biosensor devices. The development of novel nanobiocomposites with multifunctionality and improved characteristics can be considered as a developing area for scientific research.

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