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Bioinspired nanocomposites: an emerging concept of functional and ecologically sustainable hybrid materials

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Abstract

This article 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 e.g. biomedical, electronic, durable good and packaging materials. The production of nanobiocomposites by renewable and biodegradable materials helped in a range of different applications. Several drawbacks of bioplastics such as hydrophilicity, low-heat deflection, poor conductivity, and barrier properties can be efficiently overcome using nanobiocomposites. Nano-scale biocomposites present significant decrease in hydrophilicity and increase in mechanical properties as compared to neat biopolymer that fails to exhibit on its own. This approach can be used for other natural polymers to induce desired functionality. This review covers the recent trends towards nano-functional materials, renewable materials that are being applied for the production of nanobiocomposites and their applications especially in health sciences 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 biopolymer-based plastics.

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Introduction

Synthetic polymers are widely being used in everyday life for various applications. They can meet industrial and commercial market requirements e.g. durability, convenience, good performance, low cost and high variability in mechanical and barrier properties (Vert *et al.,* 2012). A significant amount of plastics is used for packaging applications, which has grown rapidly from previous two decades (Comanița *et al.,* 2016; Sommerhuber *et al.,* 2015). These synthetic polymers/plastics from petrochemical origin are highly resistant to biodegradation, causing serious threat to environment sustainability because of accumulation of non-biodegradable waste, which is increasing every year. Overdependence of fossil resources can be reduced by bioplastic production using renewable biological resources. Currently, bioplastic market is progressing with an annual growth rate of 30% of synthetic plastic market (Shen *et al.,* 2009). Many scientists are working on the production of new compounds from biological origin either by chemical modifications or by industrial biotechnological processing. Efforts are being made for the production of natural polymers or polymer building blocks using microorganisms or plants. This review aims to highlight the current advancements in bioplastics and bioinspired nanocomposites as functional hybrid materials for various industrial and biotechnological purposes and to highlight their promising healthcare applications for near future.

Polyhydroxyalkanoates (PHA) production has significantly progressed, recently it has been demonstrated that the lignocellulosic component of residual of sugarcane bagasse is an effective fermentation biomass for PHA production. The concept of utilization of waste-based biomass is promoting sustainable, bio-based economy (Tyagi *et al.,* 2018; Dietrich *et al.,* 2018). Bio-based and/or biodegradable plastic may be some biopolymers derived from and/or return to the nature.

Term 'biodegradable' and 'bio-based' are used interchangeably, but it's not correct. Bioplastic can be manufactured from biodegradable petro-based polymers, renewable material or some combinations of these. The various types of plastics available in the market are presented in Fig. 1.

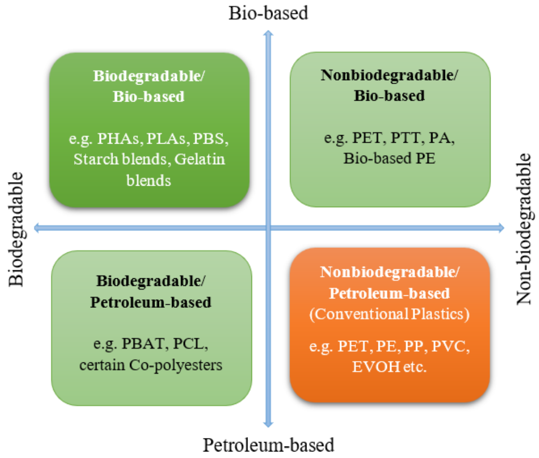

Fig. 1. Various types of plastics available in the market from origin and degradability point of view.

The production of new hybrid nanostructured materials is an emerging area among life sciences, material sciences and nanotechnology (Ozin *et al.,* 2015). From previous decade, "nanobiotechnology" has become a familiar term, used to indicate nanocomposite materials involving natural-based or a biopolymer combined with inorganic moieties and present at least on nanoscale dimension (Wang *et al.*, 2016; Cao *et al.,* 2015). 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 Zhang *et al.,* 2010).

Researchers in nanotechnology are now focusing on the development of natural-based nanocomposite materials that present outstanding characteristics of synthetic polymer-based nanocomposites (i.e. better thermal stability, improved mechanical and barrier properties) (Sanchez-Garcia *et al.*, 2010; Bordes *et al.,* 2009). In addition to these properties, nanobiocomposites also represent remarkable advantage of biodegradability, biocompatibility and, sometimes, functional characteristics provided by inorganic or biological moieties.

The increasing interest in nanobiocomposite can also be imagined by the number of publications in previous two decades as per ISI-web of knowledge – web of science database (Fig. 2).

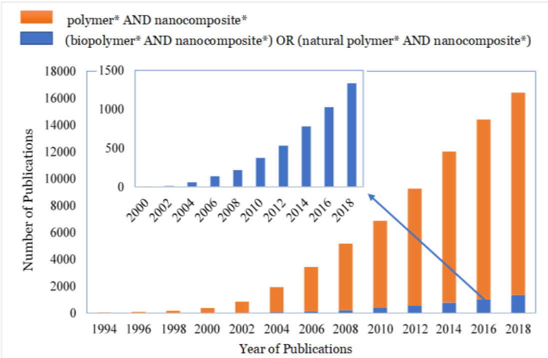

Fig. 2. Graph showing year wise number of studies related to synthetic-based nanocomposites and natural-based nanocomposites (Institute of Scientific Information (ISI) web of Science).

Several research groups are making efforts to replace petroleum-based polymers by natural, biodegradable and abundant products synthesized from renewable biomass (Han *et al.,* 2018; Xu *et al.,* 2018; Thakur *et al.,* 2015; Iwata *et al.,* 2015). Various biomacromolecules are present in the nature, that can be used as renewable biomass for the production of nanobiocomposites such as starch, cellulose and polylactic acid (PLA) as natural-based polymer are extensively being utilized for this purpose (Laadila *et al.,* 2017; Darni *et al.,* 2017; Teixeira *et al.,* 2012). Their blends with natural inorganic materials e.g. clay, carboxymethylcellulose (CMC), provides reinforcement with enhanced biodegradability and biocompatibility.

Microbes are able to decompose nanobiocomposites, giving CO_2 that is utilized by plants during photosynthesis. The applications of these biobased nanocomposites in the agriculture, biomedical or in other areas will definitely help in the maintenance of environmental sustainability. Biomacromolecules or biopolymers bearing functional moieties representing highly specific catalytic properties e.g. 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 impart multifunctionality to the nanohybrid matrix (Saba *et al.,* 2019; Cai *et al.,* 2017). The production of inorganic hybrid enzymes is an alternative way towards enzyme immobilization, useful method for the development of enzymatic reactors and biosensors.

Nanocomposites from renewable resources

Currently, a growing concern among industrialists and researchers is to use environment friendly thing, aiming to replace nondegradable substances, thereby reducing the long-term accumulation of plastic waste in the environment. Environment friendly materials having applications in agriculture, food or medicine are the major goals of several scientific studies. Petroleum-based materials are being replaced by natural/ biological and biodegradable polymers which are also renewable in natural environment e.g. cellulose, starch, polycaprolactone or PLA, are being used to synthesize biodegradable packaging materials (Mangaraj *et al.,* 2018; Rhim *et al.,* 2013). 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 of environmental damage due to petrochemical dependence.

Because of huge benefits of renewable materials with environmentally sustainable nature and an array of different applications, several scientific studies are focusing on the development of bioplastic materials with improved characteristics (Meite *et al.,* 2018; Moro *et al.,* 2017). This has led towards the production of biodegradable nanobiocomposites that represent improved properties than nonreinforced bioplastics. Natural biomacromolecules e.g. cellulose, starch and their derivatives are natural polymers used for the production of nanobiocomposite materials (Ashok *et al.,* 2018; Syafri *et al.,* 2018; Yunus and Fauzan, 2017). These materials include synthetic or natural clay minerals or modified clay minerals 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 enhanced mechanical strength of biopolymeric films.

Plasticizers are the substances added to synthetic resins to increase the flexibility and plasticity to make resulting plastic less brittle. Typically, glycerol, vegetable oil or tryethylcitrate are added as a plasticizer to bioplastic films with melting temperature near to decomposition to prevent from degradation, resulting to make good quality thermoplastic polymers. Plasticizers also contribute in 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 (Zamir *et al.,* 2018; Tabasum *et al.,* 2018). The addition of titanate as a nanofiller to PLA bioplastics result in improved biodegradation, comparable to TiO_2 (Sun *et al.,* 2018).

Although various researches comprising recent data available on nanobiocomposites have been explained above, the production of nanobased biocomposites is still in 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, e.g. LDHs would help in the improvement of mechanical and barrier properties of nanobiocomposite materials. Besides the improvement in mechanical properties, clay films also exhibit improved gas barrier and thermal stability that can be used for food packaging applications (Tang *et al.,* 2018; Opelt *et al.,* 2016).

Nanocomposites that comprise synthetic polymers and inorganic solids, the distribution of silicates in natural-based 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, e.g. the distribution of sepiolite in natural rubber causes the improvement in mechanical properties (Zaini *et al.,* 2018). Tensile strength and elastic modulus of natural rubber is increased by the addition of single walled carbon nanotubes (SWCNTs) and SiC nanoparticles-based nanocomposites, have become improved that those with just SWCNTs-based materials (Dolati *et al.,* 2018; Pati *et al.,* 2016). Multiwalled carbon nanotubes (MWCNTs) dispersion in natural rubber materials also represented the similar effect e.g. improved physical, mechanical and chemical properties of biopolymer (Wang *et al.,* 2018; Abraham *et al.,* 2016) as presented in **Fig. 3**.

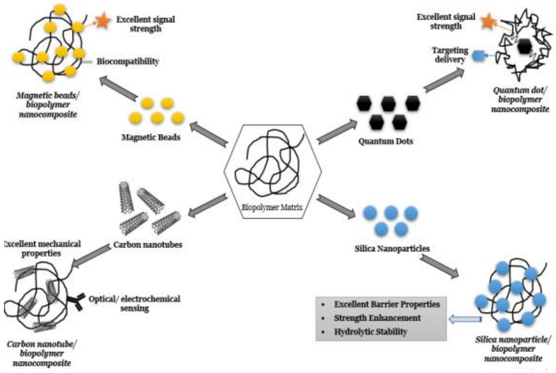

Fig. 3. The selection of nanostructure for reinforcement depending upon targeting property. Desired properties are induced in biopolymer by various nano-reinforcements.

Organic reinforcement of starch and cellulose whiskers have become sustainable replacement to other inorganic fillers e.g. nanocrystals of maize starch have been utilized as nano-reinforcement in glycerol plasticized maize starch (Garcia *et al.*, 2011; Angellier *et al.*, 2006) leading towards improvement of mechanical properties of nanocomposites (Fig. 3).

Enhancement in mechanical characteristics was also observed by the use of sodium carboxymethyl cellulose whiskers synthesized from cotton linter pulp when employed as reinforcement (Oun *et al.,* 2015). Enhancement in both young’s modulus and the tensile strength were observed, caused by the nanofiller and polymer matrix crosslinking resulting from intermolecular hydrogen bonding as shown in

Fig. 4. The interest to used environment friendly things i.e. biodegradable ones, is increasing among companies e.g. NEC and Fujitsu have started to commercialize environment 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.

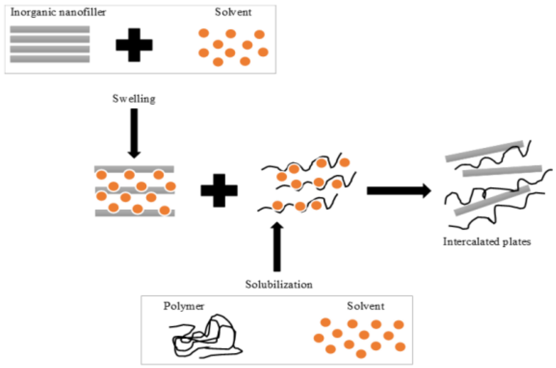

Fig. 4. Crosslinking between inorganic nanofiller and polymer matrix to form intercalated plates with improved tensile strength and modulus.

Nanobiocomposites in health sciences

Nanobiocomposites, present various applications especially in biomedical sciences like tissue engineering. The development of nanocomposites for regenerative medicine with pone implants and tissue engineering is still considered an emerging field (Huang *et al.,* 2019; Zhang *et al.,* 2016; Pina *et al.,* 2015). PLA and collagen are the most widely studied biopolymers for tissue regeneration as provide artificial support for growth of the cells. This bioresorbable scaffold require the suitable mechanical properties and sufficient macroporosity having interconnected pores to avoid collapse of implantation and to allow the transportation of metabolic substances and the nutrients and to control biodegradability (Hasnain *et al.,* 2019). Most of the articles published are related to bone repair purposes. Thyroid hormones have important role in proper body metabolism and functioning such as cardiovascular homeostasis (Qamar *et al.,* 2019) and normal kidneys function (Katz *et al.,* 1975; Basharat *et al.,* 2019). The abnormality in thyroid hormone production can cause serious health issue. Recent progress in the development of nanoscale biocomposites have led towards the development of catalase immobilized nanotubes *graft*-poly (L-lysine) for the detection of iodate and H_2O_2 (Vilian *et al.,* 2014).

Nanobiocomposites, tested and implanted for tissue regeneration include hydroxyapatite (HAp/collagen) to reproduce biocompatibility, composition and mechanical properties of bones (Ma *et al.,* 2016; Zhou *et al.,* 2015). Other biopolymers e.g. chitosan (Soundarya *et al.,* 2018; Jahangeer *et al.,* in press), PLA (Thanh *et al.,* 2015), silk fibroin (Behera *et al.,* 2017) and alginate (Naik *et al.,* 2016) 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 facilitate the propagation of osteoblasts and help in the regeneration of bones. Various synthetic techniques e.g. phase separation, gas foaming, fiber bonding, freeze-drying/emulsification have been used to synthesize foamlike nanobiocomposite with interconnected pores and suitable porosity (Yazdimamaghani *et al.,* 2017; Dziadek *et al.,* 2017).

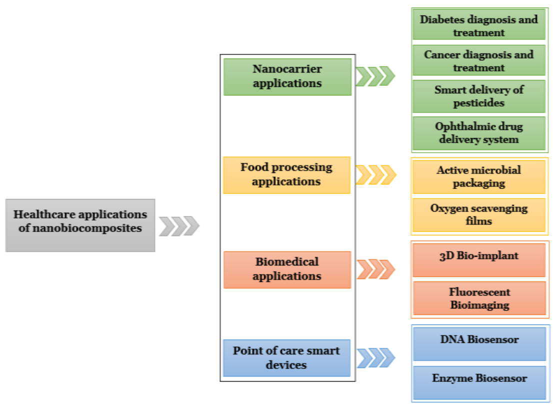

Fig. 5. Applications of nanobiocomposites in healthcare sector.

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 have been blended with polymers e.g.

collagen, giving rise to high quality multifunctional hybrid material (Cavallaro *et al.,* 2018). High affinity between sepiolite and collagen biopolymer lead towards alignment with sepiolite fibers. Degradation rate can be reduced by the treatment of this biomaterials with a crosslinker e.g. glutaraldehyde, that increase mechanical properties, enhancing longer persistence after tissue implantation (Grant *et al.,* 2018).

Nanobiocomposites also have a range of different applications, e.g. drug delivery system due to reduced dimensions and biocompatibility (Fig. 5). Various studies have been reported in past few years to study nanobiocomposites in targeted drug delivery system (Patwekar *et al.,* 2016; Kevadiya *et al.,* 2010). The use of layered double hydroxide nanostructure (LDH) transporter as a non-viral vector for gene therapy have also been studied (Andrea *et al.,* 2017). DNA intercalation in environment of Mg-Al/LDH by ion-exchange chromatography have also been conformed. Analysis by XRD showed the increase of interlayer distance, revealing LDH parallel conformation to DNA double helical structure. The DNA transfer mechanism replies upon the shielding effect induced by the negative charge of DNA structure. This conformation facilitates the transportation of hybrid structure through the cell membrane, leading to LDH dissolution at acidic pH in lysosomes, the movement of DNA to the nucleus (Wang *et al.,* 2014; Li *et al.,* 2011). Nanosized hybrid materials, suitable for drug delivery purposes, have also been extensively studied for the treatment of leukemia and diabetes using gene therapy (Huang *et al*., 2013; Calin *et al*., 2002; Li *et al*., 2011).

Future perspectives and conclusions

Nanobiocomposites are nanostructured hybrid materials blended with biopolymers. From previous few years, they have been widely studying with a number of different applications from food packaging materials to regenerative medicine. Considering their similar characteristics, this review aims to consider nanobiocomposite from an interdisciplinary purpose. There are two major purposes that have led towards the synthesis and utilization of biopolymer-based nanocomposites, replacing the conventional petrochemical-based polymer. The first one is the biodegradability of resulting hybrid materials, to manufacture environment friendly things and reduced the pollution from environment caused by plastic waste. Moreover, biocompatibility is also an important characteristic for application of these nanohybrid materials in regenerative medicine, tissue engineering or food industry.

The great efforts are being made for the production of HAP-based nanobiocomposites for bones-repair purposes. Another most important use of hybrid materials as targeted drug delivery agents, 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 biobased 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 have led towards 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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Conflict of interest

Authors declared that they have no conflict of interest.

List of abbreviation

PHA: polyhydroxyalkanoates, **PLA**: polylactic acid, **PBS**: polybutylene succinate, **PET**: polyethylene terephthalate, **PTT**: polytrimethylene terephthalate, **LDH**: lactic acid dehydrogenases, **PVC**: polyvinylchloride, **EVOH**: ethylene vinyl alcohol, **SWCNTs**: singlewalled carbon nanotubes, **MWCNTs**: multiwalled carbon nanotubes, **HAp**: hydroxyapatite, **XRD**: x-ray diffraction, **PBAT**: polybutyrate adipate terephthalate, **PCL**: polycaprolactone.

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