



Historical perspective

A critical review on the prospect of polyaniline-grafted biodegradable nanocomposite



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ABSTRACT

Among the various electrically conducting polymers, polyaniline (PANI) has gained attentions due to its unique properties and doping chemistry. A number of electrically conducting biodegradable polymers has been synthesized by incorporating a biodegradable content of cellulose, chitin, chitosan, etc. in the matrix of PANI. The hybrid materials are also employed as photocatalysts, antibacterial agents, sensors, fuel cells and as materials in biomedical applications. Furthermore, these biodegradable and biocompatible conducting polymers are employed in tissue engineering, dental implants and targeted drug delivery. This review presents state of the art of PANI based biodegradable polymers along with their synthesis routes and unique applications in diverse fields. In future, the synthesis of PANI-grafted biodegradable nanocomposite material is expected to open innovative ways for their outstanding applications.

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1. Introduction

1.1. Conducting polymers nanocomposite

Polymer nanocomposite preparation is a hybridization process between organic polymer matrices and nanoparticles with an intention to integrate their properties into a single material [1–4]. With the recent advancements in nanotechnology the need for polymers and their composites with unique properties for specific applications have gained much attention. Polymers have been considered as the excellent host matrices for composite materials [5]. Polymer blended with nanoparticles have attracted interest due to their lightweight, cost-effective process ability and unique physicochemical properties (including sensing behaviors), such as increased electric/heat conductivity, enhanced mechanical properties (stiffness and strength), magnetic properties [6] and even improved shape replicability [7,8].

Electrically conducting polymer composites are obtained when particles of good conductors (carbon black, graphite powder, carbon fiber, micro-particles of metals) are implanted into an insulating polymer matrix. Most often, such composites are used as the so-called inactive materials in electric heating elements and resistors. Recent efforts have been made to obtain active polymer composites [9–11]. The conductivity of which would be strongly dependent on external thermodynamic parameters—pressure, temperature, and others. Such materials may become the basis for a new generation of cheap large-size sensors. PANI being electrically conducting is extensively used for the preparation of electroactive and magnetic materials [12,13]. Farghali et al. prepared CuMg Ferrite [1] and integrate it with PANI and observed that the electrical conductivity of the pure PANI decreased while the saturation magnetization (M_s) and coercivity (H_c) increased with ferrite content. Khan and Khan (2007) synthesized organic–inorganic cation exchange material; poly-*o*-toluidine-Th(IV)phosphate nanocomposite by sol-gel technique [14]. Magnetic composites (magnetic polymer microspheres) have created great interest for their application in the biotechnology and medicine fields [15]. The magnetic polymer microspheres can be effectively separated and collected in the environment of the magnetic field that is appropriate for application in the areas of the cell isolation, enzyme immobilization, protein and enzyme purification and water treatment.

These nanocomposites containing conducting polymers (CPs) with superior electrical and optical properties almost similar to those metals and inorganic semiconductors which possessing ease of synthesis and good process ability. These are commonly used in electronics industry, battery technology, photovoltaic devices, light-emitting diodes, biomedical and electrochromic displays [16,17]. Among the wide range of CPs suitable for the aforementioned applications, polyaniline (PANI), polythiophene (PTh) and polypyrrole (PPy), are of particular interest because of their ease of availability, environmental stability and doping chemistry [18]. High environmental stability with low biodegradability and limited solubility due to a rigid backbone gives rise to high bioaccumulation potential of PANI over Ppy which is not sustainable [6].

1.2. Biodegradable nanocomposite

The biodegradability is an important issue as far as applications like gene therapy, drug delivery and tissue engineering are concerned [19]. Hence, there is an urgent need to develop eco-friendly biodegradable conducting polymers by incorporating a matrix of natural biodegradable polymers such as Chitosan, Gelatin, proteins or Cellulose or even synthetic non-toxic biodegradable polymers like polylactide, polycaprolactone, polyglycolide in to conducting PANI chains [20]. The biodegradable polymers have become even more important due to the excellent biocompatibility and eco-friendly nature, in almost number of fields (e.g. artificial skin, tissue engineering, sensors, packing materials, electrical conducting materials, water decontamination and disinfection) [21].

Research in the preparation and application of biodegradable nanomaterials containing graphenes, ZnO, TiO₂ and other metallic oxide nanoparticles have experienced explosive growth over recent years [22]. Graphene is a two dimensional flat monolayer of carbon atom arranged in a honey comb network [23]. Since its discovery, graphene has received great attention in numerous field e.g. in biomedicine for drug delivery [24] and gene transfection [25] biosensing [26] tumor imaging and photothermal therapy [27] nanoelectronic, nanosensing and nanoelectrochemical devices, [23] etc. Silver (Ag) nanoparticles on the other hand offer excellent electrical conductivity and antibacterial activity which can be employed in controlling diseases spreading through pathogens in water. However, no well-established data is reported about the antibacterial activity of biosensors [28]. Thus, nanocomposites of graphenes with metals and metal oxide nanoparticles not only exhibit their intrinsic properties (e.g. mechanical strength, solar absorptivity, thermal, antibacterial and photocatalytic properties etc.), but also display cooperative or synergetic effects [29]. However, due to inferior mechanical properties; poor process ability, hydrophobicity and non-biodegradability, their applications are getting limited. Thus, there is a need to develop biodegradable and electrically conducting PANI-grafted nanocomposites by incorporating biodegradable polymer matrix of PANI followed by doping nanoparticles into these biodegradable matrices.

The main advantages of biodegradable nanocomposite are; their eco-friendly nature without any harmful effect to the environment and living being. After exhausted or adsorption of environmental pollutants (metal and non-metals) on PANI-biodegradable, these nanocomposites can be recycled and easily degrade to the environment. Additionally, polyaniline-grafted biodegradable nanocomposites show outstanding applications in various fields (e.g. treatment water, biomedical applications and tissue engineering together with modified electrode and microbial fuel cell etc.) [30,31]. The conducting behaviour of PANI has potential to generate electrical signal towards cells without using any nerve growth factor.

Moreover, the most important characteristics of conducting PANI are its biocompatible and anti-corrosive characteristics which has potential to obtain free-standing nanofibers and nanomembranes that can demonstrates improved performance as compared to individual entity. Stimulation of signal to the targeted tissue and proliferation of cells using PANI-grafted biodegradable nanocomposite has been motivated researchers to synthesize innovative biodegradable materials. The improvement in physico-chemical properties (better process ability, thermally and chemical stability, optical, catalytic, magnetic and electronic properties) of nanocomposites are found due to the existence of PANI chains in their matrices [32]. Besides PANI, other organic polymer; polyglycolacid, polyvinyl alcohol, peroxyacetic acid, polyethylene glycol, polyvinyl pyrrolidone can also be employed for the synthesis of biodegradable nanocomposites [33].

1.3. Synthesis of biodegradable nanocomposite

Polymers have been considered as excellent host matrix for composite materials [1]. Synthesis of biodegradable and conducting polymer nanocomposites with nanoparticles have attracted much interest due to their lightweight, cost-effective process ability and unique physico-chemical properties, such as increased electrical conductivity, enhanced mechanical properties (stiffness and strength), sensing behaviour, and magnetic properties [7,34]. Hence, considerable efforts have been made to prepare complexes containing a polymer sensitized nanocomposite. A number of polymers are preferred for such application, however, PANI is being most important and useful. Proposed schemes for the synthesis of PANI-grafted biodegradable polymers are shown in Figs. 1 and 2 [59]. Various techniques are currently employed for the synthesis of nanocomposites based on biodegradable PANI including sol-gel, hydrothermal and chemical reduction methods while the polymers are actually prepared by either ex-situ (e.g. dispersion of the synthesized nanoparticles into a polymer solution) or in-situ processes (e.g. in situ

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