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Evaluation of poly (vinyl alcohol) based cryogel–zinc oxide nanocomposites for possible applications as wound dressing materials

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ABSTRACT

In this investigation cryogels composed of poly (vinyl alcohol) (PVA) were prepared by repeated freeze thaw method followed by in situ precipitation of zinc oxide nanoparticles within the cryogel networks. Fourier transformed infrared spectroscopy (FTIR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray diffraction (XRD), Energy dispersive X-ray spectroscopy (EDX) were used to characterize the nanocomposites. The morphologies of native PVA cryogels and PVA cryogel-ZnO nanocomposites were observed by scanning electron microscopy (SEM), transmission electron microscopy (TEM) techniques. The SEM analysis suggested that cryogels show a well-defined porous morphology whereas TEM micrographs revealed the presence of nearly spherical and well separated zinc oxide nanoparticles with diameter < 100 nm. XRD results showed all relevant Bragg's reflections for crystal structure of zinc oxide nanoparticles. Thermo gravimetric-differential thermal analysis (TG-DTA) was conducted to evaluate thermal stability of the nanocomposites. Mechanical properties of nanocomposites were determined in terms of tensile strength and percent elongation. Biocompatible nature was ascertained by anti-haemolytic activity, bovine serum albumin (blood protein) adsorption and in vitro cytotoxicity tests. The prepared nanocomposites were also investigated for swelling and deswelling behaviours. The results revealed that both the swelling and deswelling process depend on the chemical composition of the nanocomposites, number of freeze-thaw cycles, pH and temperature of the swelling medium. The developed biocompatible PVA cryogel-ZnO nanocomposites were also tested for antibacterial activities against both Gram-negative and Gram-positive bacteria.

1. Introduction

Polymeric nanocomposites are a new class of materials made with nanosized fillers possessing superior electrical, thermal and mechanical properties than those of conventional microsized filler composites due to the ultrafine dimension of the filler and large interfacial area of the nanoparticles. Nanosize inorganic particles doped into an organic polymer are called organic–inorganic hybrids. In recent years, polymer nanocomposites, especially with metallic nanofillers particularly with metal oxides have attracted extensive attention from both fundamental and applied researchers [1–3]. It is due to different physical and mechanical properties of metal nano-sized particles than those of macroscopic materials and have wide applications in diverse areas. Dispersion of metal oxide nanoparticles into polymer matrix, as the hybrid nanocomposites, not only inherit the functionalities of nanoparticles but also possess advantages of polymers such as flexibility, film integrity, conformity, mechanical strength and biodegradability.

Among polymer-metal nanocomposites, zinc oxide nanocomposites are one of the most widely used multifunctional engineered nanomaterials due to their non-toxicity, good electrical, optical and piezoelectric behaviours, environment friendly, stability in the hydrogen plasma atmosphere and low price, UV light absorption, antimicrobial, catalytic, semi-conducting, and magnetic properties [4,5].

The polymer-ZnO nanocomposites have been produced with many different matrices such as poly (vinyl pyrrolidone), poly (methyl methacrylate), poly (hydroxyethyl methacrylate), poly (ethylene glycol), low density polyethylene, poly (ethylene oxide), Nylone-6 and polyurethane [6,7]. Among various polymers, poly (vinyl alcohol) is a promising matrix which has attracted a considerable interest in biomedical applications because of its good biocompatibility and antibacterial activity. PVA is a semi crystalline, hydrophilic optically clear thermoplastic polymer and possesses excellent dielectric properties, high tensile strength, good biodegradation, high hydrophilicity, and low fouling potential and outstanding thermal and chemical stability. These properties of PVA lead well to its use in bio separation, medical, and pharmaceutical applications [8].

Recently, more and more researchers have embarked on the fundamental studies on the antibacterial activities of ZnO nanoparticles not only because they are stable under harsh processing conditions,

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but also because they are generally regarded as safe materials to human beings and animals [9]. Recent studies have shown that ZnO nanoparticles have selective toxicity to bacteria but exhibit minimal effect on human cells [10]. ZnO nanoparticles are effective for inhibiting both Gram-positive and Gram-negative bacteria. They even have antibacterial activity against spores that are high temperature resistant and high-pressure resistant [11–12]. When ZnO is incorporated in polymers it improves their mechanical and optical properties due to their high interfacial interaction between the organic moieties and inorganic nanoparticles.

However, the most significant challenge encountered in preparing ZnO-polymer nanocomposite is that the nanoparticles cannot be dispersed in polymer matrix at the nano level by conventional techniques and these particles tend to agglomerate. Therefore, a wide range of protective and stabilizing agents, including natural and synthetic polymers, dendrimers, latex particles, and hydrogels have been used to increase the stability and dispersion of metal nanoparticles in aqueous media. Out of these, hydrogels have proven to be the most promising templates and nanoreactors for in situ synthesis of nanoparticles [13]. The design and development of such hydrogels containing metallic nanoparticles have scientific and technological research interests in recent years due to their unique and versatile properties [14–16]. Hydrogels offer large free spaces between the cross linked networks in the swollen stage that serve for nucleation and growth of nanoparticles and act as nanoreactors [17,18].

Hydrogels represent hydrophilic polymeric networks capable of imbibing large quantities of water without being soluble under physiological conditions of pH, temperature and ionic strength due to chemical or physical cross linking between individual polymeric chains [19]. Crosslinks between polymeric chains can be formed by covalent, electrostatic, hydrogen bonds or dipole–dipole interactions [20]. Hydrogels have been used in numerous applications, including biosensors, bioreactors, bio separators, tissue engineering, and drug delivery, due to their excellent biocompatibility [21,22]. Hydrogels are normally prepared by thermal, redox, or radiation induced polymerization of a monomer in the presence of a suitable crosslinker, but these traditional methods have several disadvantages, such as toxic effects of cross linkers, loss in the biocompatibility of the entrapped agent, precise control over crosslinking and therefore, to some extent limit the biological applications of these hydrogels. Therefore, hydrogels with good biocompatibility, biodegradability, nontoxicity and mechanical strength are highly desirable.

With these considerations in mind the present study follows a cryogenic approach of solidification of PVA, known as freeze thaw method, to avoid chemical cross linking process. This physical cross-linking phenomenon by successive freezing thawing cycles is based on the existence of regular pendant hydroxyl groups on PVA that are able to form crystallites by strong inter-chain hydrogen bonding [23]. Advantages of physically cross-linked hydrogels include potential bioactivity, nontoxicity, non-carcinogenicity, high elasticity and the excellent biocompatibility, mechanical strength, porosity of the resulting polymer [24]. Cryogels made from natural and synthetic polymers have emerged as promising materials to fabricate new macro porous architectures which may find novel applications in biomedical and biotechnological fields.

Thus, this study aims to design a PVA cryogel-ZnO nanocomposite by repeated freeze-thaw method and study their water sorption, deswelling, blood compatibility, mechanical and antibacterial behaviours.

2. Materials and methods

2.1. Materials

Poly (vinyl alcohol) (PVA) (degree of hydrolysis 98.8% Mol. Wt. 70,000 Da) was purchased from Merck, India and used without any pre-treatment. Other chemicals such as zinc chloride, potassium hydroxide were purchased from Merck, India. All chemicals were of analytical grade and doubly distilled water was used throughout the experiments.

2.2. Methods

2.2.1. Preparation of PVA cryogels

The freeze-thaw method was adopted in preparing cryogels of PVA as reported elsewhere [25].In a typical experiment, 2 g of PVA was dissolved in 25 mL of distilled water under hot condition (80 °C) with continuous mechanical stirring until a homogeneous viscous mixture was obtained and transferred into a Petri dish then kept at −20 °C for 24 h. The frozen gels were then thawed for 2 h at room temperature (25 °C) and again kept at −20 °C for freezing. Such freezing thawing cycles were repeated at least five times so that the whole mass was converted into soft, spongy and elastic gel known as cryogel. The gels so prepared were purified by equilibrating them in distilled water for 24 h so that all unreacted chemicals were leached out and the composition of the remaining solution were measured spetrophotometrically and chemically no significant amount of PVA was found in the solution. The swollen gels were cut into smaller discs and dried at room temperature and stored in air-tight plastic bags.

2.2.2. In situ synthesis of zinc oxide nanoparticles in prepared PVA cryogel

An in-situ precipitation method was followed for impregnation of zinc oxide nanoparticles into the cryogel matrix. Briefly, various circular discs of prepared PVA cryogel membrane were treated by 5 M potassium hydroxide solution for 12 h to hydrolyze the film surfaces. After removal from the potassium hydroxide solution, the films were rinsed with distilled water and then blown with dry air. Then, the base treated discs were immersed into aqueous zinc chloride solution at room temperature for 24 h to incorporate zinc ions into the films through an ion-exchange reaction between potassium and zinc ions and then the films were rinsed by distilled water to remove the unbound residual zinc chloride solution and finally treated films were dried by heating slowly in air oven for 6 h. The reactions involved in the synthesis of zinc oxide nanoparticles are,

$$ZnCl_2 + 2NaOH \rightarrow Zn(OH)_2 + 2Na^+ + 2Cl^-. \quad (1)$$

$$Zn(OH)_2 \rightarrow ZnO + H_2O \quad (2)$$

2.3. Characterization and analysis

2.3.1. FTIR spectroscopy

The infrared spectral analysis of the prepared native PVA cryogel and nano zinc oxide loaded cryogels was performed on FTIR-8400, Shimadzu Spectrophotometer. The spectra were obtained in the range of 4000 to 400 cm^{-1} with a resolution of 2 cm^{-1}.

2.3.2. Thermo gravimetric analysis (TGA)

The thermal properties of the PVA cryogel ZnO nanocomposites were evaluated by using Perkin Elmer Thermal analysis instrument in a temperature range 50–1010 °C at a heating rate of 10 °C/min under N_2 atmosphere (20 mL/min).

2.3.3. Scanning electron microscopy (SEM and EDX)

Surface morphological features of the prepared cryogel ZnO nanocomposite were investigated by recording their scanning electron micrographs on a JEAOL JXA-840 scanning electron microscope (SEM). The elemental analysis of the nanocomposite was performed by a SEM equipped with an energy dispersive X-ray spectrum (EDX), which can provide a rapid qualitative and quantitative analysis of the elemental composition of the prepared sample.