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Morphological, electrical & antibacterial properties of trilayered Cs/PAA/PPy bionanocomposites hydrogel based on Fe_3O_4-NPs

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ABSTRACT

Bionanocomposites hydrogel based on conducting polymers were successfully fabricated from chitosan/polyacrylic acid/polypyrrole (CS/PAA/PPy) as well as the magnetite nanoparticle (Fe_3O_4–NPs) was prepared via co-precipitation method. In addition, different ratios of Fe_3O_4–NPs were added to the prepared bionanocomposites to enhance the antimicrobial and the electrical conductivity of the prepared conductive hydrogel. Furthermore, the morphology, the swelling percent, antimicrobial activity and the dielectric properties of the prepared conducting bionanocomposites hydrogel were investigated. The antibacterial activities of the experienced microbes were improved with the increasing the loading of Fe_3O_4-NPs in conducting Bio-nanocomposites hydrogel. Moreover, the DC-conductivity was examined and our resulted indicated that the DC-conductivity was enhanced by increasing the loadings of Fe_3O_4-NPs compared to that of the pure CS/PAA as well as CS/PAA/PPy.

1. Introduction

Biopolymers are renewable resources produced during the life cycle of plants, animals, bacteria and fungi. They are characterized by their complex structures, low dispersity index and easy degradation. Chitosan is a natural polymer derived from deacetylation of chitin, which may be obtained from crustaceans, insects, fungi, etc. it is consider the second abundant polysaccharide next to cellulose. Chitosan has one primary amino and two free hydroxyl groups for each C6 building unit. Because of the easy availability of free amino groups in chitosan, it carries a positive charge and thus in turn reacts with many negatively charged surfaces/polymers. Chitosan owns hydrogel-like properties through a reaction with acrylic acid or methacrylic acid (Corradini, de Moura, & Mattoso, 2010) or with glutaraldehyde as a crosslinking agent. The form of a chitosan hydrogel can be used in a wide range of applications such as wastewater treatment (Crini, 2006), separation membrane (Won, Feng, & Lawless, 2002), food packaging (Youssef, El-Sayed, Salama, El-Sayed, Dufresne, 2015; Youssef, E.L-Sayed, E.L-Sayed, Salama, & Dufresne, 2016) wound healing (Arvanitoyannis, 1999; Arvanitoyannis, Nakayama, & Aiba, 1998), and a drug delivery system (Nunthanid et al., 2004).

Lately, conducting polymers such as polypyrrole and polyaniline have predictable great attention owing to their easy synthesis, controlled conductivity, and good stability (Kwon, Park, Yoon, & Jang, 2012; Youssef, 2014; Youssef & El-Sayed, 2018; Youssef, Mohamed et al., 2017). Conducting polymer hydrogels as a novel class of materials that possess both the swelling properties and the electrical properties, have been extensively investigated (Guo, Finne-Wistrand, & Albertsson, 2011; Xiao, He, & Che, 2012). Composite hydrogels of polyaniline/polyacrylamide, polypyrrole/polyacrylic acid have been elaborated from adsorption of monomer inside a polymer network followed by the polymerization of the monomer according to a radical or electrochemical process (Lira & Cordoba de Torresi, 2005; Xu et al., 2006). Interfacial polymerization has also been carried out to synthesis conducting polymer hydrogels. In this case, polyaniline could grow from the solution–gel interface to the gel interior, maybe leading to a gradient concentration material and the non-homogeneous hydrogel in bulk (Blinova, Trchova, & Stejskal, 2009; Dai, Qing, Wang, Shen, & Lu, 2010). Moreover, in the above methods, the conducting polymer is entrapped in the cross-linked hydrophilic polymer matrix as the main network in the hydrogel, resulting in a possible migration of the conducting polymer from the hydrogel matrix during the process of

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swelling-shrinking or upon exposure to pH change.

In order to further impart new functionalities to chitosan for expanding its application fields, the use of suitable nanoparticles is highly demanded. Nanoparticles (NPs) and their applications are a growing area of technology and assessment of nanomaterials is the key to nanotechnology

Magnetic nanoparticles are attractive materials not only in the field of magnetic recording but also in the areas of biological and medical applications (Iida, Takayanagi, Nakanishi, & Osaka, 2007). One of the encouraging particles is the iron oxide nanoparticle with several kinds and derivatives: magnetite (Fe_3O_4) and hematite (Fe_2O_3). These are extensively used as materials for drug carrier (Yang, Park, Yoon, Huh, & Haam, 2006), drug release (Zhou et al., 2009), cancer therapy (Hu, Neoh, & Kang, 2006), hyperthermia, magnetic separation, magnetic resonance imaging (MRI) (Ma & Liu, 2007), proton exchange membrane (Brijmohan & Shaw, 2007), and sensor (Luo et al., 2010). Conversely, magnetite nanoparticles are the greatest studied materials owing to their response to magnetic field through the super-paramagnetic behavior at room temperature with high saturation magnetization. In addition, their non-toxicity and high biocompatibility are also suitable for biotechnology areas (Kumar, Inbaraj, & Chen, 2010).

It became well known that the dielectric properties play an important role in assessing the functions of biomaterials. Their dielectric properties are probing their chemical structure, composition, material processing as well as their historical and environmental parameters (Ahmed, Ramaswamy, & Raghavan, 2008; Wolf, Gulich, Lunkenheimer, & Loidl, 2012; Youssef et al., 2016). Chitosan is considered to be one of the most important biopolymer due to its unique properties such as: its high sorption capacity, low toxicity bio-compatibility with living tissues, bio-inertness, and bio-degradability. This makes it applicable in variety of fields of applications, such as drug delivery, tissue engineering, electrochemical sensing and actuation. Recently, considerable attention is continuously being given to study the molecular dynamics and electrical properties of chitosan (Bobritskaya, Castro, Gorokhovatsky, & Temnov, 2013; Bobritskaya, Castro, & Temnov, 2013; Viciosa, Dionisio, Silva, Reisand, & Mano, 2004; Viciosa, Dionisio, Silva, & Mano, 2004).

In the current work we study the morphology as well as the antibacterial properties of the conductive hydrogel (CS/PAA/PPy) based on Fe_3O_4–NPs, in addition broadband relaxation spectroscopy will be employed to study the dielectric and electrical properties of the prepared conductive bionanocomposites.

2. Materials and methods

2.1. Materials

Chitosain (CS), acrylic acid (AA) and Pyrrole (Py) were purchased from Sigma–Aldrich (USA) and used without further purification. Sodium dodecyl benzene sulfonate (DBSA), Ethanol, methanol and ammonium hydroxide were purchased from Fluka. Potassium persulfate (PPS), ferrous chloride tetrahydrate and ferric chloride anhydrous were obtained from S.D. fine-chem Ltd.

2.2. Preparation of magnetite nanoparticles (Fe_3O_4–NPs)

The magnetite nanoparticles were prepared via the chemical co-precipitation method by the following 1.5 g of $FeCl_2{\cdot}4H_2O$ and 3.0 g of $FeCl_3$, with the molar ratio of ferric ion to ferrous ion in the solution of 2.45, were dissolved in 100 ml of deionized water under a nitrogen gas flow with vigorous stirring at various temperatures (0–90 °C). A 10 ml of 25 wt% NH_4OH was added to the solution, since the solution color changed from orange to black rapidly. The magnetite nanoparticles were filtered and thoroughly washed with deionized water to remove chloride ions, and finally dried in a vacuum at 80 °C for 24 h (Carvalho, Henriques, Ferreira, Godinho, & Cruz, 2013).

2.3. Preparation of chitosan/polyacrylic acid (CS/PAA) hydrogel

The CS-PAA hydrogel were obtained by polymerization of AA in CS solution in two-step process. In the first step, chitosan was dissolved in two different concentration 2% and 4% (wt/v) acrylic acid aqueous solutions (100 ml) for 12 h under magnetic stirring. The CS concentration used in synthesis was 2% (wt/v). In the second step, 0.185 and 0.37 mmol of PPS was added to the solution, respectively, with continued stirring, until the solution became clear. The polymerization was then carried out at 70 °C under magnetic stirring for 2 h leading to the formation of CS/PAA (1/1 and 1/2) nanoparticles, which was then cooled in an ice bath (Guo, Liu, Hong, & Li, 2010).

2.4. Preparation of polypyrrole (PPy)

Polypyrrole was synthesized by chemical oxidative polymerization technique. The chemical polymerization was carried by dissolving DBSA (25 g) and pyrrole monomer (10 g) in 200 ml of water under constant stirring at ambient temperature then a solution of $FeCl_3{\cdot}6H_2O$ (18 g/100 ml) was added dropwise to start the oxidation polymerization. The synthesis was allowed to proceed at 5–7 °C. The polypyrrole was collected by filtration and rinsed with distilled water then ethanol then dried at 45 °C.

2.5. Preparation of CS/PAA/PPy/Fe_3O_4-NPs bionanocomposites

The PPy was dispersed in CS/PAA (1/1 and 1/2) solution, where PPy to CS was 1:1 wt, and then polyethylene glycol 5 ml where added and stirring by homogenizer at 10000 rpm for 10 min. After that 1%, 3% and 5% (g/PPygm) of Fe_3O_4-NPs were added to CS/PAA/PPy solution and stirring at 10000 rpm by homogenizer for another 10 min. The prepared CS/PAA/PPy/Fe_3O_4-NPs bionanocomposites solution are poured into biter dish and dried in oven at 45 °C for 24 h to get CS/PAA/PPy/Fe_3O_4bionanocomposites films. The recipes of all achieved runs are collected in Table 1.

2.6. Characterization

2.6.1. Infrared (IR) spectral analysis

FT-IR spectra of nanomaterial and paper cheat were recorded in the range of 400–4000 cm^{-1} on Shimadzu 8400S FT-IR Spectrophotometer.

2.6.2. X-ray diffraction (XRD)

The crystal structure of the filler powders was determined using a Philips X-ray diffractometer (PW 1930 generator, PW 1820 goniometer,) equipped with Cu Kα radiation (45 kV, 40 mA, with $\lambda = 0.15418$ nm). The scans of the analysis were run in 2θ range of 5–80° with step size of 0.02 and step time of 1s. The lattice d-spacing was calculated from the (200) and (310) reflections in the diffraction patterns via Bragg's equation. ($n\lambda = 2d \sin\theta$).

Table 1
The chemical composition of bionanocomposites films.

Sample code	CS (g)	AA (g)	PPy (g)	Fe_3O_4-NPs (g)
CS/PAA	1.00	1.00	0.00	0.00
CS/PA/PPy	1.00	1.00	1.00	0.00
CS/PA/PPy1	1.00	1.00	1.00	0.01
CS/PA/PPy3	1.00	1.00	1.00	0.03
CS/PA/PPy5	1.00	1.00	1.00	0.05
PPy	0.00	0.00	0.00	0.00
CS/2PAA	1.00	2.00	0.00	0.00
CS/2PAA/PPy	1.00	2.00	1.00	0.00
CS/2PAA/PPy1	1.00	2.00	1.00	0.01
CS/2PAA/PPy3	1.00	2.00	1.00	0.03
CS/2PAA/PPy5	1.00	2.00	1.00	0.05