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Synthesis, characterization and antimicrobial activity of biodegradable conducting polypyrrole-graft-chitosan copolymer

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ABSTRACT

In this study, polypyrrole-graft-chitosan (PPy-*g*-CS) copolymer was chemically synthesized and its structural and morphological properties characterized by FTIR, UV–vis, SEM, XRD, TGA and zeta-potential techniques. The results revealed that there were strong interactions between PPy and CS chains. The electrical conductivity of CS increased to semiconducting range by grafting. The crystallinity and thermal stability of PPy-*g*-CS copolymer improved when compared to CS. The copolymer was tested against various bacterial and fungal strains at various concentrations and results obtained were compared with the reference antibiotics. The results indicated that the antibacterial activity of PPy-*g*-CS copolymer was stronger than CS and PPy alone. The antibacterial activity of the PPy-*g*-CS copolymer observed to increase with rising concentration, and showed stronger activity against bacteria than *Penicillin* (10 mg), *Rifampicin* (5 mg) and *Trimethoprim* (25 mg), whereas showed equipotent activity with *Amikacin* (30 mg) and *Erythromycin* (15 mg) antibiotics.

1. Introduction

Polysaccharides, as a class of natural macromolecules, have the tendency to be extremely bioactive, and are generally derived from agricultural feedstocks or crustacean shell wastes. Chitosan (CS) is a linear polysaccharide derived from chitin, second most abundant organic compound next to cellulose. The application potential of CS is multidimensional, such as in food and nutrition, biotechnology, materials science, drugs, pharmaceuticals, agriculture, environmental protection, and recently in gene therapy too [1]. As a natural renewable resource, CS possesses unique properties such as biocompatibility, biodegradability, non-toxicity, and excellent film-forming ability. Chitosan has both reactive amino and hydroxyl groups that can be used to chemically alter its properties under mild reaction conditions [2]. Chemical modification of CS is an important topic for production of multifunctional biodegradable materials by blending, composite preparation or graft copolymerization. In contrast to blends and composites reported in the literature, graft copolymerization of monomers onto CS back bone produce covalently bonded new materials which are branched macromolecules and behave as a single structure, which brings together some advantages for potential applications with their unique functionality and solubility [3,4]. Among these applications, CS based antimicrobial materials have been attracting much attention from the food industry as a barrier against moisture, oxygen, flavor and oil [5]. The benefit of using biodegradable polymer is their potential of decomposing naturally over short periods of time in nature. So it is very important to concert the material from biostable to biodegradable structure. Harish and Tharanathan [6] reported acrylonitrile and methylmethacrylate graftings onto CS back-bones with grafting yields of 249% and 276%, respectively. Jin et al. reported that a Schiff base of CS prepared with citral worked well under high-intensity ultrasound, showed better antimicrobial activities than CS and also increased with an increase in Schiff base concentration [7].

Conjugated polymers have attracted enormous attentions from both science and technology as semiconductors and electroactive materials for their applications in batteries, molecular electronic devices, sensors, solid phase extractions and light emitting diodes etc. [8]. However, the use of conducting polymers in biological applications is often limited because of their insolubility in common solvents, thereby making the processing difficult [9]. They can be used in the form of powders, aqueous dispersions, as

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coatings on variety of substrates. Also, ability to be doped in reduced or oxidized form (redox properties) of conducting polymers has facilitated its usefulness in certain biological applications [10]. Seshadri and Bhat reported that polyaniline coated conductive cotton fabrics have potent antibacterial and antifungal activities [11]. The incorporation of conducting polymers into natural polymers can enhance the performance of both the 'host' and the 'guest' thereby leading to interesting physical and chemical properties.

The most common polymers synthesized and utilized for various applications are polypyrrole (PPy), polythiophene (PT), polyaniline (PAni) and their derivatives. Among the conducting polymers, PPy has attracted intense attention due to its environmental stability, ease of synthesis, exciting chemical, electrical, electrochemical and optical properties [12]. Heterocyclic derivatives of pyrrole were reported to be having important synthetic and biological activities [13,14]. To the best of our knowledge, there are a few reports in the literature on antibacterial and antifungal activities of conducting-biodegradable copolymers. Based on these observations, present study was focused on the investigation of antibacterial and antifungal biological activities of PPy and CS hybrid graft copolymer. Some physical, structural, and morphological characteristics of this conducting graft copolymer were investigated by means of various techniques and the results obtained were compared with CS and PPy.

2. Experimental

2.1. Materials

Chitosan, $\overline{Mw} = 3.0 \times 10^5$ g mol^{-1} and with 75–85% degree of deacetylation, was obtained from Aldrich with analytical grade. $FeCl_3$ was provided from Merck and used as oxidizing agents. Pyrrole was also supplied from Merck and used as monomer after vacuum distillation. N-methylpyrolidone (NMP), ethanol, acetic acid (HAc), HCl, NaOH and all the other reagents were provided from Aldrich with analytical grade and used as received. The reference antibiotic discs were obtained from Oxoid, Thermo Fisher Scientific.

2.2. Synthesis of conducting polypyrrole-graft-chitosan copolymer

Conducting and biodegradable PPy-*g*-CS copolymer was synthesized by chemical oxidative radicalic polymerization method and their molecular structure is shown schematically in Fig. 1. For this purpose, CS was dissolved in a flask in 1 wt.% HAc. In another flask, definite amount of pyrrole monomer was also dissolved in 1 wt.% HAc and added into the above mentioned solution. After 1 h of mixing, $FeCl_3$($n_{oxidant}$:$n_{monomer}$ = 3:2) was added dropwise into the reaction reactor and kept stirring under nitrogen atmosphere at 0–10 °C for 16 h. The solution formed in black color was neutralized with 0.5 M $NaOH_{(aq)}$ to precipitate CS groups in the copolymer. To remove any impurities present, recovered crude graft copolymer was washed with NMP, hot distilled water and distilled water, respectively and dried in a vacuum oven at 70 °C for 48 h degree of grafting (GD%) was gravimetrically determined as the percentage of the weight increase of CS using the following equation:

$$GD(\%) = \frac{W_g - W_0}{W_0} \times 100 \quad (1)$$

where W_g and W_0 are the weights of grafted and pristine CS chains, respectively. Thus, conducting graft copolymer of PPy and CS was obtained and its antimicrobial activity against five bacteria and two funguses was evaluated.

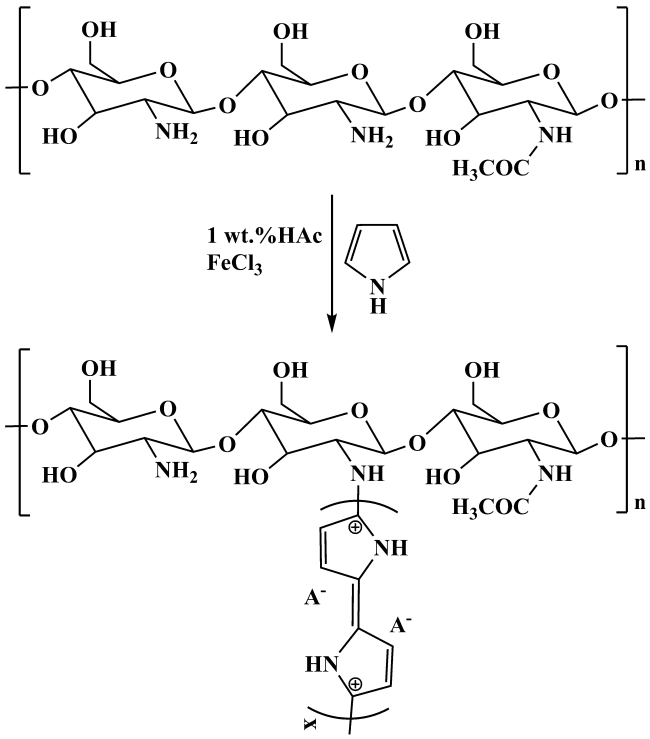

Fig. 1. Synthesis of PPy-*g*-CS copolymer.

2.3. Characterizations

The CS, PPy and PPy-*g*-CS were dried in a vacuum oven and ground milled to obtain fine particles and homogeneous size distributions using a Retsch MM400 model milling machine (Germany) and subjected to the following characterizations.

Particle sizes of the samples were determined by dynamic light scattering (DLS) using Malvern Zeta-Sizer Nano ZS (England). The PPy-*g*-CS copolymer was subjected to solubility tests in water, acetic acid, silicone oil, $CHCl_3$ and NMP. Apparent densities of the samples were calculated using their pellet's masses and volumes. Electrical conductivity measurements for the sample pellets were performed at room temperature by using a FPP-460A model four-probe electrical conductivity-measuring instrument (Entek Electronic Co., Turkey). FTIR spectra of the samples were conducted as KBr pressed discs on a Perkin Elmer Spectrometer BX FTIR system (England). The samples were dissolved separately in 20 mL of NMP and UV–vis absorbance spectra were recorded using Perkin Elmer (Model Lambda 20, USA) spectrophotometer. The surface morphology of the polymers were examined by using a JEOL JSM 5500LV (Japan) SEM. XRD patterns of powder samples were obtained using D8 advance X-ray diffractometer (Bruker, Germany) with a CuKα radiation (λ = 0.15418 nm) at 40 kV and 50 mA at 25 °C. The relative intensity was recorded in the scattering range of 1–10° at a scanning speed of 1° min^{-1}. Thermal analyses of the samples were performed with a Perkin Elmer Diamond TGA/DSC thermal analysis instrument (USA). The specimens were heated at a heating rate of 10 °C min^{-1} under N_2 atmosphere from room temperature to 600 °C. Although organic solvents and their mixtures were also tried, it was not possible to dissolve and record ^{1}H NMR spectrum for PPy-*g*-CS copolymer. The zeta-potential (ζ) measurements were performed with a Malvern Zeta-sizer Nano ZS which works with Laser Doppler Electrophoresis technique using folded capillary cell equipped with gold electrodes. The optic unit contains a 4 mW He–Ne laser (λ = 633 nm).

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