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Biodegradable polypyrrole/dextrin conductive nanocomposite: Synthesis, characterization, antioxidant and antibacterial activity

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ABSTRACT

Combination of a natural biodegradable polymer with a synthetic polymer offers excellent capability in advanced functional materials. For this purpose, biodegradable conductive nanocomposites based on polypyrrole/dextrin have been synthesized by in situ polymerization of pyrrole in the presence of dextrin activated in acidic medium. The nanocomposites were characterized by Fourier transform infrared (FT-IR), Ultraviolet–visible (UV–vis), X-ray diffraction (XRD), differential scanning calorimetry (DSC) and field emission scanning electronic microscopy (FESEM). The conductivity of nanocomposites was investigated by four probe method. The prepared nanocomposites were analyzed for antioxidant activity using 2,2-diphenyl-1-picrylhydrazyl assay (DPPH). Our results demonstrated that the conductivity and antioxidant activity of nanocomposites were increased by increasing the amount of polypyrrole in nanocomposite matrix. The nanocomposites were analyzed for antibacterial activity against Gram-positive and Gram-negative bacteria. The results indicated that the nanocomposites are effective against all of studied bacteria and nanocomposite 1 effectiveness is higher for *Pseudomonas aeruginosa* while nanocomposite 2 is effective against *Staphylococcus aureus*. In addition, in vitro biodegradability study of the polypyrrole/dextrin composites with different weight ratio was investigated in soil burial degradation. The result demonstrated that the composites are biodegradable under natural environment in range of 30.18–74.52% degradation. The observed physical properties of the polypyrrole/dextrin nanocomposites open interesting possibilities for novel applications of electrically conducting polysaccharide-based composites, particularly those that may exploit the antimicrobial nature of the polypyrrole/dextrin nanocomposites.

1. Introduction

During the last decade, the use of inherent conducting polymers such as polyaniline (PANI), polythiophene (PTh), polypyrrole (PPy), polyfuran (PFu), poly(p-phenylene vinylene) (PpPV) and poly(acetylene) (PAc) has received a great deal of attention because of their immense variety of physical and electro-conductive properties [1–6]. Among them, PPy has been received a considerable amount of attention because of its high electrical conductivity, environmental stability and favorable physicochemical properties [7–12]. PPy can be synthesized by chemical oxidation or electrochemical polymerization of pyrrole (Py) in various organic solvents and in aqueous media [13,14]. In a chemical oxidative polymerization of Py, many oxidants such as, ferric chloride ($FeCl_3$), ferric perchlorate (Fe $(ClO_4)_3$), and ammonium peroxydisulfate (APS) have been used [15].

However, practical application of PPy has been largely limited due to the poor mechanical property and processability [16,17]. To improve the structural and physical properties, several studies have been accomplished to prepare blends or composite materials containing PPy [18–20]. By coating of conductive PPy or in situ polymerizing of Py on substrate such as fibers, MWCNT, and graphite, new composite materials with diverse properties were produced [21–23]. Along these, recently a series of novel conducting composites of PPy/cellulose with high galvanostatic cycling stability for use in flexible energy devices i.e. batteries, higher thermal stability in nanofibrous membrane, enhanced ion absorption capacity, and tunable electrochemical properties have been developed. Also, porous conducting PPy–nanocellulose composites have been introduced as high capacity electrochemical control solid state material for extraction and release of DNA oligomers [24–31].

Nowadays, extensive researches in synthesis of eco-friendly and high performance materials are new tendency to develop novel conductive composites. In recent years, there have been considerable attractions in the synthesis of conducting/biopolymer composites that contain different synthetic and biological polymers.

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More recently, electroactive PPy/Chitosan composite nanospheres and highly conducting PPy/Cellulose nanocomposite films with enhanced mechanical properties were introduced [32,33].

Dextrin (Dex) is known as a low-molecular-weight polysaccharide composed of D-glucose units connected by α-(1 → 4) or α-(1 → 6) glycoside bonds [34]. It is produced by the hydrolysis of starch or glycogen, and widely used as adhesives in the food and textiles industries [35–37]. Owing to cheapness, biodegradability and biocompatibility, Dex found great potential in biocompatible composites production [38].

In our previous work, synthesis of biodegradable conductive composite of polyaniline/starch was introduced [39]. The main goal of the current study was to synthesize and evaluate the biological activity of the conductive nanocomposites based on Dex and PPy which obtained via in situ polymerization. The influence of PPy content on the conductivity and antioxidant activity of the nanocomposites were investigated. The nanocomposites were evaluated for their antibacterial activity against Gram positive and Gram negative bacteria. In addition, the soil biodegradability of the synthetic nanocomposites was also studied using soil burial condition. These conducting nanocomposites were characterized by means of FT-IR, XRD, UV–vis, DSC and FESEM techniques.

2. Experimental

2.1. Materials

Pyrrole (Merck) was purified by double distillation under reduced pressure and stored in a refrigerator before use. White dextrin and 2,2-diphenyl-1-picrylhydrazyl (DPPH) were purchased from Aldrich Company. Ammonium peroxydisulfate (APS) and dodecylbenzenesulfonic acid (DBSA) were purchased from Merck Company.

2.2. Measurements

FT-IR analysis was carried out on a Bruker Tensor 27 spectrometer (Bruker, karlsrohe, Germany). UV–vis absorption spectra were measured in transmission by a Cecil 5000 UV-Vis spectrometer. The X-ray diffraction (XRD) spectra were recorded on an X'pert Philips X-ray photoelectron spectrometer (The Netherlands) with nonmonochromated Mg Kα radiation as the excitation source. Differential Scanning Calorimetry (DSC) analyses of the prepared polymers were performed with a LENSES STAPT-1000 calorimeter (Germany) with scanning up to 600 °C at a heating rate of 10 °C/min. Field Emission Scanning Electron Microscopy (FESEM) was recorded on a Hitachi S4160 instrument. Electrical conductivity of the compressed pellets of polymer and nanocomposite was measured by four probe method under laboratory condition.

2.3. Synthesis of PPy/Dex nanocomposite

The PPy/Dex nanocomposites were synthesized by in situ polymerization of Py in the presence of aqueous Dex solution in acidic medium under magnetic stirring in an inert atmosphere and ice bath. In a typical synthesis, in a 250 mL three-necked flask equipped with inlet and outlet of inert gas, 100 mL hydrochloric acid (1.0 M) and 2 mL of double distilled Py were mixed. Then, 1 g Dex was added into the above solution and the mixtures were cooled down to 0–5 °C while being stirred mechanically for 30 min.

The solution was degassed with argon. A solution containing 2.5 g of APS in distilled water (20 mL) was added in dropwise within 30 min. The reaction mixture was stirred below 5 °C for 10 h to complete the polymerization. After completing of reaction, the resulting black precipitate was filtered and washed several times with methanol and distilled water. The resulting PPy/Dex nanocomposite was dried overnight at 60 °C under vacuum. Then, the PPy/Dex nanocomposites were undoped with aqueous ammonia (5 wt%) and washed exhaustively with water until the filtrate became neutral. The filter cake was dried in vacuum at 50 °C. For redoping of the nanocomposite, about 1.5 g of the PPy/Dex nanocomposite powder was transferred into 150 mL of DBSA (1.5 M) while being stirred magnetically for 3 h. Finally, the redoped PPy/Dex nanocomposite was filtered, washed with water and dried in vacuum at 60 °C for 24 h.

2.4. Antioxidant activity

One of the conventional methods to determine the antioxidant activity of materials is to evaluate the scavenging activity of DPPH as a stable free radical. The DPPH free radical with an odd electron gives a maximum absorption at 517 nm (purple color). When the composites react with DPPH, the free radical becomes paired off in the presence of a hydrogen donor and reduces to the DPPHH or converts to DPPH anion through electron transfer reaction. Consequently, the absorbance decreases for the DPPH. Antioxidant activity was measured using the DPPH assay according to the already reported method with slight modification [40].

Briefly, 25 mg of DPPH was dissolved in 100 mL ethanol and then 1 mL of this solution was mixed with 1, 2, 3, 4 and 5 mg of Dex, PPy and nanocomposites. The reaction mixture was shaked for 30 s and incubated in dark condition at 25 °C with humidity of 60% for 15 min, after which the wavelength scanning was performed using a UV–vis spectrophotometer. The absorbance was measured at 517 nm for different concentration at different time intervals at room temperature. Decrease in the absorbance of the DPPH solution indicates an increase of the antioxidant activity. The DPPH inhibition was calculated using the formula:

$$\%\ \text{of DPPH inhibition} = \frac{A_b - A_s}{A_b} \times 100$$

where A_b is the absorption of the blank (DPPH + EtOH) and A_s is the absorption of the sample (DPPH + Sample + EtOH).

2.5. Soil biodegradability test

The soil burial degradation test of the synthetic nanocomposites was conducted in aerobic soil condition in the presence of natural microorganisms. The test nanocomposites were prepared by compression molding with a thickness of 1.5 mm under pressure of 2 MPa. Tablets with 14 mm in diameter were buried in the soil (pH = 7.5) in which the relative humidity maintained was 60–70% by spraying water and the temperature was 28–30 °C in the humidity chamber. The buried nanocomposites were monitored for 60 days. The compound decomposition by soil microorganisms was monitored during this period using a digital camera. In addition, degradability was evaluated by measuring the weight loss of tablets and the results were reported as Mean ± SD after three repeats.

2.6. Antibacterial activity assay

The in vitro biocidal screening, antibacterial activities of the compounds were assayed using Kirby–Bauer disk diffusion method where a filter disk was impregnated with the compounds and placed on the surface of inoculated agar plates [41]. Dex, the synthesized PPy and nanocomposites (2 g) were dissolved in 100 mL of DMSO and then filter sterilized using a 0.22 μm Ministart (Sartorius).

The antibacterial activity of the compounds was investigated against four bacterial species. Test organisms included *Escherichia*