



Full Length Article

Surface modification of chitin and chitosan with poly(3-hexylthiophene) via oxidative polymerization



Thien An Phung Hai, Ryuichi Sugimoto*

School of Environmental Science and Engineering, Kochi University of Technology, Miyanokuchi, Tosayamada, Kami, Kochi 782-8502, Japan

ARTICLE INFO

Article history:

Received 7 September 2017

Received in revised form 27 October 2017

Accepted 27 October 2017

Available online 28 October 2017

Keywords:

Chitin

Chitosan

Poly(3-hexylthiophene)

Surface modification

Contact angle

ABSTRACT

In the present work, the modification of biomaterials such as chitin and chitosan were successfully prepared by directly grafting poly(3-hexylthiophene) (P3HT) to their surfaces using simple oxidative polymerization with FeCl_3 . The thermal stability and crystallinity of grafted chitin and chitosan changed upon grafting with P3HT. The build-up of π - π structure from the P3HT on the surface of chitin and chitosan resulted in the appearance of UV-vis absorption and fluorescence emission peaks in the range from 500 to 600 nm. Introducing P3HT to the surface of chitin and chitosan improved significantly the electrical property of chitin and chitosan with the increase in conductivity from 10^{-9} to 10^{-7} S/cm. Furthermore, the usual behavior of hydrophilic surface of chitin and chitosan that turned to hydrophobic with water contact angle of 97.7° and 107.0° , respectively in the presence of P3HT. The mechanism for graft reaction of P3HT to chitin and chitosan was also proposed and discussed.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Chitin and chitosan are crucial biopolymers having special chemical reactivity and physical properties, and are found in diverse applications of drug delivery system, antibacterial activity and other systems [1–3]. During two decades for researches of novel functional and sustainable chitin/chitosan-based materials, there have been various efforts to enhance the physical and chemical properties of this polysaccharide by modification. “Grafting through” [4–6], “grafting onto” [7–9], and “grafting from” [10] are three frequent strategies for polymer modification. The difference types of techniques for modification of chitin and chitosan have been reported. Grafting methyl methacrylate (MMA), 4-vinylpyridine (4-VP), acrylic acid (AA), methacrylic acid (MAA) onto chitin/chitosan in water or aqueous acetic acid have been done by using ceric ion initiation [11–14]. Fenton’s reagent, a combination of potassium persulfate (KPS) and other reducing agents (ferrous ammonium sulfate (FAS), CuCl_2 , MnCl_2 , ...) have been used to graft vinyl monomer onto chitin/chitosan [15–19]. Chitin and chitosan have also been modified with polystyrene (PS) by free radical mechanism using ammonium persulfate (APS) [20,21]. Radical grafting by ionizing radiation

(γ -radiation or electron beam) has been used to graft copolymerization chitin/chitosan with various vinyl monomer [22,23]. The grafting vinyl monomer onto chitin has been carried out using tributylborane (TBB) [24]. The surface modification of chitin nanocrystals with poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) was successfully accomplished using chloridization reaction that improved the lipophilicity of chitin nanocrystals [25]. The high capacity adsorbent property of the chitin fibers functionalized with the uranyl-selective amidoxime group for extraction uranium from seawater has been reported [26]. Hydrophobic modification on surface of chitin for highly effective separation of oil from water was synthesized successfully [27]. Amphiphilic surface of chitosan was achieved by grafting of hydrophilic polyacrylamide and hydrophobic polystyrene for ability reversible switching in polar and nonpolar medium [28], and an improvement of hydrophilic property of chitin nanofiber by graft polymerization with acrylic acid was accomplished [29].

Although conducting polymers has superior electrical conductivity, the physical and mechanical properties are not very good [30–32]. To enhance the physical and mechanical properties of these conducting polymer, blending mixture of conducting and conventional polymer and grafting conducting polymer on typical polymer have been prepared [32,33]. Both of chitin and chitosan are the second most abundant biopolymer with vital merits such as biocompatible, biodegradable, high mechanical strength and non-toxicity [34]. Recently, advances in cooperation between the conjugated polymer and biomaterials have driven new interest in

* Corresponding author.

E-mail addresses: an.phthien@gmail.com (T.A.P. Hai), sugimoto.ryuichi@kochi-tech.ac.jp (R. Sugimoto).

engendering materials with novel functionalities, further opening the scope of applications such as biosensors, bioelectronics, tissue engineering, and biofuel cells [35–38]. The use of conjugated polymers together with biopolymer could provide the good properties of final material such as processability and conductivity. The electrical conductivity can be measured in the in-plane direction (surface conductivity) or in the through-the-thickness direction (volume conductivity) [39]. The properties and electrical conductivity of some conventional conducting polymer as well as hybrid composites of conducting polymer have been reported [39].

The substituted polyaniline/chitosan composite was synthesized using ammonium persulfate as an oxidant in an aqueous acid [40]. Grafting of polyaniline onto the radiation crosslinked chitosan has been applied for sensor and electrodes of polymeric batteries [41]. Chitosan-graft-polyaniline based hydrogels was synthesized by simple oxidative method using ammonium persulfate, resulting in high and reversible swelling properties in hydrogel with intrinsic conductivity [42]. Electron beam radiation has been used to synthesize chitin-polyaniline nanocomposite [43]. Polythiophene chitosan magnetic nanocomposite was applied for extraction of triazine herbicides from aquatic media [44]. Grafting polypyrrole onto chitin was accomplished using ammonium peroxy disulphate (APS) as an initiator [32]. However, the main purposes of these works were to make the composite materials due to the insolubility of polythiophene, polypyrrole, and polyaniline. The goal of our research is to graft conjugated polymers such as poly(3-hexylthiophene) directly to chitin and chitosan.

Oxidative polymerization of thiophene was discovered three decades ago and is now widely used for its ease of polymerization [45–52]. Herein, we report a new methodology for directly grafting conjugated polymers to chitin/chitosan by oxidative polymerization using FeCl_3 . In this report, P3HT is used as conjugated polymers due to its unique properties such as high solubility, high efficiency emission in a wide variety of colors, low operating voltage [53], performance enhancement of organic light-emitting diode (OLEDs) [54]. The resulting grafted chitin and chitosan were characterized by Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD), UV–vis, Fluorescence, Transmission electron microscopy (TEM) Energy dispersive X-ray (EDX), ^1H -nuclear magnetic resonance (H NMR), Gel permeation chromatography (GPC), contact angle, and Thermo gravimetric (TG).

2. Materials and experiment

2.1. Chemicals

Chitin and chitosan are in flake form and were purchased from Tokyo Chemical Industry Ltd (TCI). Commercial chitosan from TCI has degree of deacetylation (DD) in 80% and medium molecular weight with a viscosity of 0.5% chitosan in 0.5% acetic acid solution at 20 °C from 200 to 600 mPa. All chitin and chitosan were kept and stored in the UNICO UN 650F mode box under an atmosphere of argon, as they are hygroscopic. 3-Hexylthiophene (3HT), monomer and anhydrous FeCl_3 were obtained from Tokyo Chemical Industry Ltd and used without any further purification. Solvents such as chloroform, hexane and methanol were analytical grade, purchased from Wako Pure Chemical Industry Ltd and used as received. Hexane, medium for graft reaction was dried by standing over 4A molecular sieves for 8 h, and purged with argon gas for 20 min before use.

2.2. Measurement

The UV–vis spectrophotometers were analyzed using the diffuse reflectance measurement in a Jasco V-650 UV–vis spectrometer,

set in absorbance photometric mode with a UV/Vis bandwidth of 2.0 nm, a data interval of 1.0 nm, and scan speed of 400 nm min^{-1} . Fluorescence spectra were recorded at room temperature on a Jasco spectrofluorometer FP-8300. Thermo gravimetric analyses (TG) were measured on a Hitachi Thermal Analysis System STA 7200 RV in air from 20 to 700 °C at a flow rate of 25 ml min^{-1} and heating rate of 10 °C min^{-1} . ^1H NMR spectra (400 MHz) and IR spectra were conducted on a Bruker Ascend 400 spectrometer and a Jasco FT/IR – 480 Plus, respectively. X-ray diffraction patterns were recorded with Cu-K α radiation (X-ray wavelength: 1.5418 Å) in steps of 0.02° over the 2 θ range of 5–70° from a Rigaku Smartlab diffractometer equipped with a D-tex detector. Transmission electron microscopy (TEM) images were observed using a JEOL JEM-2100F microscope. Energy dispersive X-ray (EDX) mappings and line scan spectra were recorded on an Oxford INCA Energy TEM 250. Gel permeation chromatography (GPC) was measured on a system equipped with a Jasco PU-2080 Plus pump and a Jasco RI-2031 plus intelligent RI detector. Contact angle was analyzed on portable contact angle analyzer PGX. For contact angle measurement, the samples are prepared as followed step: the chitin/chitosan and grafted chitin/chitosan are compressed to form flat and smooth samples. Electrical conductivity was carried out with an Agilent 34401A 6 $^{1/2}$ Digit Multimeter resistometer by a four-probe method

2.3. Grafting and sample preparation

All reactions in this work were carried out in an oven-dried Schlenk flask with a stopcock under an argon atmosphere. An amount of 0.3 g chitin and 0.3 g FeCl_3 were dispersed in 7 ml hexane with a magnetic stirrer. After the mixture was performed ultrasound treatment for 20 min, the suspension of chitin and FeCl_3 in hexane was cooled to 0 °C in an ice bath. The hexane (3 ml) solution of 3HT (100 mg, 0.6 mmol) was dropped into a magnetically suspension of chitin and FeCl_3 . The reaction was conducted for 2 h at 0 °C under an argon atmosphere. The stoichiometric ratios of 3HT to FeCl_3 is 1:4. The reaction was terminated by adding methanol. The obtained product was washed with methanol by Soxhlet extract apparatus to remove any residual FeCl_3 , and then it was extracted with chloroform to eliminate free poly(3-hexylthiophene) (P3HT) homopolymer using a Soxhlet extractor. Grafting of 3-hexylthiophene to chitosan were conducted using a similar procedure to that described above. A series of grafting reaction of 3-hexylthiophene to chitin and chitosan in different ratio n ($n = \text{weight of } \text{FeCl}_3 / \text{weight of chitin or chitosan}$) was conducted as above. Finally, the final products were dried under vacuum for 12 h. The grafted chitin/chitosan are hereinafter referred as P3HT-g-chitin and P3HT-g-chitosan.

3. Results and discussion

3.1. Images of P3HT-g-chitin and P3HT-g-chitosan

In this work, grafting poly(3-hexylthiophene) to chitin and chitosan were conducted in hexane. There are two simultaneous reactions of both oxidative self-polymerization of 3-hexylthiophene and graft polymerization of 3-hexylthiophene to chitin and chitosan during the graft reactions of poly(3-hexylthiophene) to chitin and chitosan. Soxhlet extraction was used to remove ungrafted 3-hexylthiophene homopolymer from the grafted chitin and chitosan. After drying in vacuum for 12 h, the final products were collected and showed in Figs. 1 and S1 (Supporting information). The different color of chitin and chitosan before and after grafting with P3HT can be clearly observed with the naked eye.

Download English Version:

<https://daneshyari.com/en/article/7836182>

Download Persian Version:

<https://daneshyari.com/article/7836182>

[Daneshyari.com](https://daneshyari.com)