



Influences of solution plasma conditions on degradation rate and properties of chitosan



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ABSTRACT

In this work, the effects of solution plasma conditions on the degradation rate and properties of chitosan are investigated. Various types of electrodes including tungsten (W), copper (Cu), and iron (Fe) were used. The treatment time and the applied pulse frequency of the bipolar supply varied from 0 to 210 min and 15 to 30 kHz, respectively. The plasma-treated chitosan was characterized by GPC, XRD, FT-IR, and fractionation analysis. The results showed that after plasma treatment for 210 min, the molecular weight of chitosan decreased remarkably, when compared to those of untreated samples. The plasma treatment of chitosan using Fe electrode and high pulse frequency strongly promoted the degradation rate of chitosan. The XRD analysis showed that the crystallinity of plasma-treated chitosan was destroyed. FT-IR analysis revealed that the chemical structure of chitosan was not changed by solution plasma treatment. Solution plasma treatment of chitosan using an Fe electrode provided the highest %yield of water-soluble chitosan.

Industrial Relevance: In this study, the solution plasma process is introduced to treat chitosan in order to prepare low-molecular-weight chitosan. According to our finding, the solution plasma could be a potential method for the preparation of low-molecular-weight chitosan and chitoooligosaccharides. Since the solution plasma is generated under mild conditions (i.e., the reaction proceeds at room temperature and ambient pressure), therefore, it is very attractive for the degradation of polysaccharide polymer and applicable to industrial materials process such as medicine, food, chemical industry, and cosmetics. In addition, we expected that plasma technology could be used instead of conventional enzymatic treatment and chemical treatment which was high cost and contamination process.

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1. Introduction

Chitosan, the deacetylated derivative of chitin, is one of the abundant, nontoxic, renewable, biodegradable polymers. It is composed of β -1,4-linked 2-amino-2-deoxy-D-glucopyranose (GlcN) and 2-acet-amido-2-deoxy-D-glucopyranose (GlcNAc) units and widely presented in exoskeletons of shellfish and insect (Jayakumar, Menon, Manzoor, Nair, & Tamura, 2010; Jayakumar, Prabaharan, Sudheesh, Nair, & Tamura, 2011; Shahidi, Arachchi, & Jeon, 1999). Therefore, chitosan has received much attention for various applications such as food, pharmaceuticals, biomaterials, drug delivery, medicine, and cosmetics. However, the high molecular weight, high viscosity, and low solubility in water of chitosan derived from chitin are

the main problems and restrict its application. Several techniques including chemical, physical, and enzymatic treatment have already been performed to degrade the high-molecular-weight chitosan into low-molecular-weight chitosan (LMWC) which exhibits water solubility, bioactivities including antitumor, antimicrobial, as well as anti-inflammatory properties (Chang, Tai, & Cheng, 2001; Choi, Ahn, Lee, Byun, & Park, 2002; Xie, Hu, Wei, & Hong, 2009; Yue, Yoa, Wei, & Mo, 2008). Among these techniques, enzymatic treatment is an effective process to achieve LMWC. However, the main drawbacks of this process are low production yield and slowly enzymatic reaction. In addition, since it is operated under mild conditions and requires multiple steps, especially enzyme preparation and product purification, therefore, this process is considered as the complicated and high cost process.

Electrical discharge in the liquid phase is known as “solution plasma process (SPP)” and has recently been proposed to be an effective process. Currently, SPP has received much attention for various applications such as carbon material synthesis, surface modification of polymers, wastewater treatment, and degradation of organic compounds (Takai,

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2008). An important advantage of SPP is the production of highly active species, especially hydroxyl radicals (OH^\bullet) is obtained (Potocký, Saito, & Takai, 2009; Prasertsung, Damrongsakkul, & Saito, 2013; Prasertsung, Damrongsakkul, Terashima, Saito, & Takai, 2011). Moreover, since the solution plasma is generated under mild conditions and not involved any strong chemical reagents, therefore, the removal of chemical residue is not required. The present study was aimed to study the effects of SPP conditions on the degradation rate and properties of the degraded chitosan product. For this purpose, the degradation of β -chitosan was carried out by SPP with different types of electrodes and the applied pulse frequency. The degradation rate of chitosan was calculated by kinetic study. The properties of chitosan including the molecular weight, chemical structure, crystal structure, and solubility were investigated. The properties of degraded products were characterized by GPC, FT-IR, and XRD. Moreover, the water solubility of degraded product was then determined by fractional analysis.

2. Materials and methods

2.1. Materials

β -Chitosan was prepared according to a procedure similar to that described by Sashiwa et al. (2003). In short, the ground squid pen was soaked in 2 N NaOH solution overnight to deproteinize. The deproteinized product were then treated with a similar solution at 100 °C for 4 h followed by excessive washing with distilled water to remove more residual protein. The β -chitin samples were deacetylated with 25% NaOH (112.5 °C) to achieve β -Chitosan with the degree of deacetylation and average molecular weight of 90% and 1.3×10^5 Da, respectively. Acetic acid, acetone, hydrochloric acid, and sodium hydroxide were used as received. All of the chemicals, reagents, and solvents used were of analytical grades. The water used was distilled and deionized.

2.2. Solution plasma experiment

β -Chitosan was dissolved in 1 M acetic acid to obtain 0.5% w/v chitosan solution and placed in the glass reactor. The setup of solution plasma system, modified from our previous study (Prasertsung et al., 2013), is shown in Fig. 1. The solution plasma was operated at atmospheric pressure. The solution plasma was produced at the fixed voltage and pulse width of 1.6 kV and 2 μ s, respectively. Various types of electrodes including tungsten (W), copper (Cu), and iron (Fe) were used. The applied pulse frequency of bipolar power supply and treatment time of the solution plasma were within the ranges of 15–30 kHz and 0–210 min, respectively. The uniformity of chitosan solution to contact with the plasma was controlled using magnetic

stirrer. After the plasma treatment of chitosan was completed, the plasma-treated and untreated chitosan were characterized.

2.3. Characterization of plasma-treated chitosan

Optical emission spectroscopy (OES) was used to monitor the light emitted from the plasma in the wavelength range of 200–1000 nm. To characterize the species in plasma-treated chitosan solutions, the emission was detected through the quartz glass window with an optical fiber placed 1 mm in front of the glass chamber. Data were acquired with Avantes software (Baroch, Anita, Saito, & Takai, 2008).

Gel permeation chromatography (GPC, Water 600E, Waters, USA) was used to characterize the apparent molecular weights of plasma-treated and untreated chitosan solutions. The ultrahydrogel linear 1 column was used. The concentration of chitosan solutions was 0.4 mg/ml. Eluent and chitosan sample solutions were filtered through 0.45 μ m Millipore filters. The flow rate was maintained at 0.6 ml/min at 30 °C. The pullulans (M_w , 5900–708,000 Da) were used as standard samples.

The crystal structure of both before and after degradation was characterized by X-ray diffractometer (Shimadzu Lab XRD-6000, Japan). The plasma-treated and untreated chitosan solutions were cast into mold to form thin films. X-ray diffraction patterns of the plasma-treated and untreated chitosan films were measured with a $\text{CuK}\alpha$ target at 40 kV and 50 mA. The relative intensity was recorded in the scattering range (2θ) of 5–40°.

FT-IR spectroscopy (Digilab, FTS 7000 Series, USA) was used to characterize the chemical composition of plasma-treated and untreated chitosan samples. All of the ATR-FT-IR spectra were collected using 64 scans in the range of 4000–400 cm^{-1} at a resolution of 4 cm^{-1} .

2.4. Fractionation of chitosan solution

Fractionation of chitosan solution was conducted in order to determine the amount of water-soluble and water-insoluble chitosan of plasma-treated and untreated samples. In short, the pH of plasma-treated and untreated samples was adjusted to approximately 7.5 using NaOH solution. The precipitated chitosan was then removed by centrifuging at 5000 rpm for 30 min. The obtained sample was coded as the first precipitate (water-insoluble chitosan). The supernatant was then mixed with an equal volume of acetone to give a second precipitate (water-soluble chitosan). The first and second precipitate chitosan samples were dried at 60 °C for 24 h. The % yields of the first and second precipitate were calculated following Eq. (1):

$$\% \text{yield} = (W_1/W_2) * 100 \quad (1)$$

where W_1 and W_2 are the weights of dried precipitate chitosan and the chitosan added to acetic acid (untreated chitosan), respectively.

3. Results and discussion

3.1. The effects of types of electrodes on reactive species generated during plasma treatment

The emission spectra of plasma-treated chitosan solution, determined at a treatment time of 1 min, as a function of type of electrodes compared, are presented in Fig. 2. The spectrum of the plasma-treated chitosan solution using W electrode showed strong peaks at wavelengths of 456.0, 656.5, and 777.3 nm, corresponding to H_γ , H_α , and O-radicals, respectively (Baroch et al., 2008). These reactive species could be generated by the decomposition of water molecules, the medium used in this study, caused by ionic current (Wattanaphanit, Heo, & Saito, 2014). After Cu and Fe electrodes were introduced, the additional spectrum peaks were observed. In the case of Cu electrodes, the peaks were present at the wavelengths of 324.5 and 521.8 nm, corresponding to Cu I, while the Fe electrode displayed the peaks at the wavelengths of

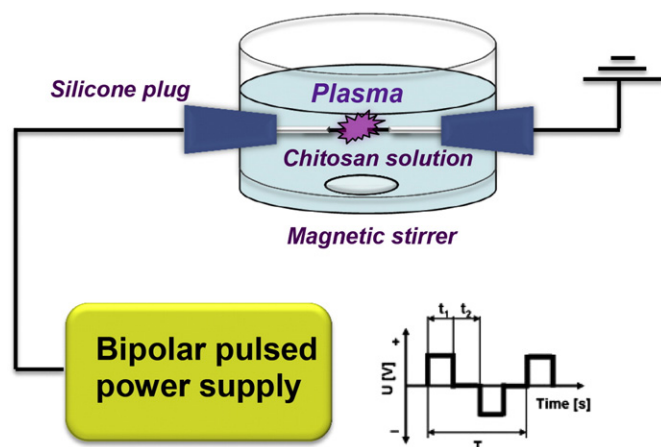


Fig. 1. Schematic diagram of solution plasma process.

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