Radiation Physics and Chemistry 80 (2011) 837–841

Contents lists available at ScienceDirect

Radiation Physics and Chemistry

journal homepage: www.elsevier.com/locate/radphyschem

Physicochemical and functional characteristics of radiation-processed shrimp chitosan

F.C.K. Ocloo [a,*], E.T. Quayson [b], A. Adu-Gyamfi [a], E.A. Quarcoo [a], D. Asare [a], Y. Serfor-Armah [c], B.K. Woode [b]

[a] Biotechnology and Nuclear Agriculture Research Institute, Ghana Atomic Energy Commission, P.O. Box LG 80, Legon, Ghana
[b] Department of Biochemistry, University of Cape Coast, Cape Coast, Ghana
[c] National Nuclear Research Institute, Ghana Atomic Energy Commission, P.O. Box LG 80, Legon, Ghana

ARTICLE INFO

Article history:
Received 10 December 2010
Accepted 3 March 2011
Available online 10 March 2011

Keywords:
Chitosan
Irradiation
Molecular weight
Viscosity
Degree of deacetylation

ABSTRACT

The effects of gamma irradiation on chitosan samples were determined in terms of physicochemical and functional properties. Shrimp chitosan was extracted from shell using a chemical process involving demineralization, deproteinization, decolorization and deacetylation. Commercial snow chitosan was also used. Samples (in a solid state) were given irradiation dose of 25 kGy at a dose rate of 1.1013 kGy/h in air and 0 kGy samples were used as controls. Results showed that moisture contents were between 8.690% and 13.645%. There were no significant differences ($P > 0.05$) in the degree of deacetylation of the chitosan samples. Significant differences ($P < 0.05$) were observed in the viscosity and viscosity-average molecular weight of the chistosan samples. Viscosity and molecular weight decreased when the samples were given the irradiation dose of 25 kGy. Chitosan samples had low antioxidant activity compared with BHT. Water binding capacity ranged from 582.40% to 656.75% and fat binding capacity was between 431.00% and 560.55%. Irradiation had a major effect on the viscosity and the viscosity-average molecular weight of the chitosan samples.

1. Introduction

Chitin is composed of β(1–4) linked units of the amino sugar *N*-acetyl-glucosamine, and is the main source of production of chitosan, which is used in a number of applications (No and Meyers, 1995). Over the last several years, chitinous polymers, especially chitosan, have received increased attention as one of the promising renewable polymeric materials for their extensive applications in the pharmaceutical and biomedical industries for enzyme immobilization and purification, in chemical plants for wastewater treatment and in food industries for food formulations as binding, gelling, thickening and stabilizing agent (Knorr, 1984). Earlier studies by No et al. (2000), Cho et al. (1998) and Wu and Bough (1978) have demonstrated that the physicochemical characteristics of chitosan affect its functional properties, which also differs due to crustacean species and preparation methods. High molecular weight and viscosity limit its use in various applications. Gamma radiation is known to cause main chain scissions in polysaccharides and decreases the viscosity and average molecular weight of the polymers (Rao et al., 2006).

It has been reported that low molecular weight radiation-processed products show antibiotic, antioxidant and plant-growth-promoting properties in some countries. As its unique polycationic nature, chitosan has been used as an active material such as antifungal activity (Ben-Shalom et al., 2003; Hirano and Nagano, 1989; Kendra et al., 1989; Roller and Covill, 1999; Uchida et al., 1989), antibacterial activity (Choi et al., 2001; Chung, et al., 2003; Helander et al., 2001; Jeon and Kim, 2000; Liu et al., 2001), antitumor activity (Koide, 1998; Mitra et al., 2001; Qin et al., 2001, 2004; Suzuki et al., 1986) and plant growth (Chmielewski et al., 2007). Attempts have been made to reduce the cost of production of chitosan through depolymerization of chitosan by radiation or chemical degradation combined with irradiation method (Chmielewski et al., 2007).

Intensive work has been done in countries such as China, Japan, Indonesia, Korea, Malaysia, Philippines, Thailand and Vietnam in relation to radiation processing of polymers and the applications of the radiated-processed products in agriculture, healthcare, industry and environment for the benefits of end-users (IAEA, 2008). A few studies have been undertaken in Ghana in the area of radiation processing and characterization of chitin and chitosan from crab shells (Emi-Reynolds et al., 2007), as well

* Corresponding author. Tel.: +233 244 467195; fax: +233 302 400807.
E-mail addresses: fidelis_ocloo@yahoo.com, ocloofid@hotmail.com (F.C.K. Ocloo).

0969-806X/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.radphyschem.2011.03.005

as Neutron Activation Analysis of chitin and chitosan from crab shells (Banini et al., 2007). The general aim of this study is to evaluate the effect of gamma radiation on the physicochemical and functional properties of the shrimp chitosan.

2. Materials and methods

2.1. Sample collection and preparation

Shrimp was purchased from fishermen at the Tema fishing harbor. The shellfish was cooked and the shells were separated from the other components. The shells were then dried in the oven at 60 °C for overnight. The dried shells were ground in moulinex blender, sieved to a particle size of 90 μm and then packaged in polyethylene bag for storage at ambient temperature until used.

2.2. Isolation/production of chitosan

The method described by No et al., 1989 with some modifications was used.

2.2.1. Demineralization (DM)

The shrimp shells were demineralized with 1 N HCl for 30 min at ambient temperature with a solid to solvent ratio of 1:15 (w/v) (No et al., 1989) with constant stirring, and then filtered in vacuum. The filtrate was washed for 30 min with tap water and then oven-dried.

2.2.2. Deproteinization (DP)

The demineralized shells were deproteinized with 3.5% (w/w) NaOH solution for 2 h at 65 °C with constant stirring at a solid to solvent ratio of 1: 10 (w/v) (No et al., 1989). The sample was filtered in vacuum, and the filtrate was washed with tap water for 30 min and then oven-dried.

2.2.3. Decoloration (DC)

Shrimp shells (also referred to as demineralized, deproteinized or shrimp chitin) were decolorized with acetone for 10 min and dried for 2 h at ambient temperature, followed by bleaching with 0.315% (v/v) sodium hypochloride (NaOCl) solution (containing 5.25% available chloride) for 5 min at ambient temperature with a solid to solvent ratio of 1: 10 (w/v), based on dry shell (No et al., 1989). Samples were then washed with tap water and dried in vacuum for 2–3 h until the powder was crispy.

2.2.4. Deacetylation (DA)

Removal of acetyl groups from chitin was achieved by refluxing for 5–6 h at 100 °C using 50% concentrated sodium hydroxide solution (NaOH) with a solid to solvent ratio of 1:15 (w/v). The resulting chitosan was washed to neutrality with tap water, rinsed with hot distilled water (90 °C), filtered and dried at 60 °C for 24 h in an oven.

Commercial crab chitosan sample was obtained from Heppe Medical HnC^{+} GmbH, Germany.

2.3. Radiation

Gamma Irradiation Facility at the Radiation Technology Centre (RTC) of the Ghana Atomic Energy Commission was used. The facility uses ^{60}Co source (SLL-515, Hungary). Samples (in a solid state) were irradiated at 25 kGy, with a dose rate of 1.1013 kGy/h in air and the absorbed dose confirmed by Fricke's dosimetry.

3. Analytical procedures

3.1. Physicochemical characteristics

3.1.1. Moisture content

Moisture content of the samples was determined by the gravimetric method (AOAC, 1990).

3.1.2. Degree of deacetylation (DD)

Films prepared from the sample were used to study the degree of deacetylation (DD). Chitosan films were prepared according to the method mentioned by Baxter et al. (1992) with slight modifications. Chitosan films were prepared by casting 1.0% w/v chitosan in 1% acetic acid solutions, followed by drying in an oven for 12 h, the chitosan films were deprotonated by washing 3 times with methanolic ammonia, followed by distilled water and finally methanol. The chitosan films were kept in desiccators for 16 h, and then placed in sealed plate before scanning. The spectra of the chitosan were obtained using Fourier Transform Infrared Spectroscopy (FTIR-8400S CE, Shimadzu Corporation, Japan) with a frequency range of 4000–400 cm^{-1}. The degree of deacetylation was calculated using the baseline by Sabnis and Block (1997).

3.1.3. Viscosity-average molecular weight (Mv)

For the determination of viscosity-average molecular weight (Dalton), the chitosan was dissolved in a mixture of 0.1 M acetic acid/0.2 M sodium chloride solvent at 25.0 °C and then a Ubbelohde glass capillary viscometer (size 1, Poulten, Selfe & Lee Ltd., England) was used to measure the intrinsic viscosity (η) (No et al., 2000). The Mark–Houwink equation relating intrinsic viscosity with empirical viscometric constants $K=1.81\times10^{-3}$ cm^3/g and $a=0.93$ for chitosan was used to calculate the molecular weight using this equation: $\eta=KM^a$.

3.1.4. Viscosity

The method described by Fernandez-Kim (2004) with few modifications was used. Viscosity of the chitosan was determined with a Brookfield viscometer (Model DV-II+Brookfield Engineering Laboratories, Inc., Stoughton, MA). Chitosan solution was prepared in 1% acetic acid at 1% concentration on a dry basis. Measurement was made in duplicates using spindle number 2 at 50 rpm on solutions at 28 °C with values reported in centipoises (cPs) units.

3.1.5. Antioxidant activity

Antioxidant/free radical-scavenging activity of chitosan sample was estimated according to the method of Blois (1958) with some modification. The chitosan sample of various concentrations (2.5, 5.0, 7.5 and 10.0 μg/mL) were prepared using 1% acetic acid. The samples were added into the 0.004% 2,2-diphenyl-1-picrylhydrazyl (DPPH) free radical (Sigma–Aldrich Co., St. Louis, MO). The mixture was shaken and incubated for 30 min at room temperature. The absorbance was then measured at 517 nm using a spectrophotometer (model UV-1601PC, Shimadzu Co., Tokyo, Japan). The DPPH radical-scavenging capacity was estimated based on the difference in absorbance with or without samples and expressed as a percentage of DPPH scavenging. Butylated hydroxytoluene (BHT) was used to compare the DPPH free radical-scavenging activity of chitosan samples.

3.2. Functional characteristics

3.2.1. Water binding capacity (WBC)

Water binding capacity (WBC) of the chitosan samples was measured using a modified method of Wang and Kinsella (1976).