LWT - Food Science and Technology 57 (2014) 172–180

Contents lists available at ScienceDirect

LWT - Food Science and Technology

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

Evaluation of chitosan nanoparticles as a glazing material for cryogenically frozen shrimp☆

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ARTICLE INFO

Article history:
Received 19 July 2013
Received in revised form
9 December 2013
Accepted 22 December 2013

Keywords:
Frozen storage of shrimp
Lipid oxidation of shrimp
Aerobic
Yeast and molds counts of shrimp

ABSTRACT

The potential of chitosan (CH) combined with sodium tripolyphosphate (TPP) nanoparticles as a glazing material for shrimp was investigated. Two CH–TPP nanoparticles glazing solutions were prepared: (1). A solution containing CH–TPP nanoparticles with 0.25 (g/100 mL) CH and 0.083 (g/100 mL) TPP (25CH–TPP) and (2). A solution containing CH–TPP nanoparticles with 0.5 (g/100 mL) CH and 0.167 (g/100 mL) TPP (50CH–TPP). Frozen shrimp samples were glazed with 25CH–TPP, 50CH–TPP, CH, TPP, acetic acid, and/or distilled water and then stored at −21 °C for 30 days. Glazed and non-glazed shrimp (NG) samples were analyzed for moisture content, glazing yield, weight loss, color, cutting force, thiobarbituric acid reactive substances (TBARS), yeasts, molds, coliforms and aerobic counts after 1, 3, 5, 20, and 30 d storage. Triplicate experiments were conducted and data statistically analyzed ($\alpha = 0.05$). Glazed shrimp had higher moisture than NG after 30 d storage. Among the glazes, 25CH–TPP and 50CH–TPP were the most effective in controlling lipid oxidation and reducing aerobic counts and yeasts and molds in shrimp.

1. Introduction

Shrimp is among the top-five most popular seafoods consumed in the United States. The 2010 US shrimp harvest totaled 117,469 metric tons which had a value of 413.98 million dollars (NOAA, 2010). Normally, raw shrimp is stored in the frozen state because it is highly perishable. According to Boonsumrej, Chaiwanichsiri, Tantratian, Suzuki, and Takai (2007), the quality of frozen foods deteriorates during storage due to factors like the rate of freezing and thawing, storage temperature, temperature fluctuations, freeze–thaw abuse during storage, transportation, and retail display. Lipid oxidation, protein denaturation, sublimation and recrystallization of ice crystals can occur during frozen storage of shrimp which results in off-flavors and odors, rancidity, dehydration, weight loss, loss of juiciness, drip loss and toughening (Londahl, 1997). Microbial spoilage can also occur during storage (Bhobe & Pai, 1986).

To suppress quality changes of frozen food products during storage, polysaccharides and proteins have been used as glazing materials (Sathivel, Liu, Huang, & Prinyawiwatkul, 2007). According to Debeaufort, Quezada-Gallo, and Voilley (1998), biodegradable glazing materials act as a barrier to control moisture transfer and oxygen uptake of frozen foods. Several glazing ingredients have been tested to extend the shelf life of seafood products including whey protein isolates, alginate, green tea extract and chitosan (Sathivel et al., 2007; Stuchell & Krochta, 1995; Sundararajan et al., 2011).

Chitosan [β-(1,4)-2-amino-2-deoxy-D-glucopyranose] is a natural polysaccharide that is a partially deacetylated derivative of chitin, the second largest source of carbohydrates on Earth (Muzzarelli et al., 2012). Due to its biochemical and mechanical properties, chitosan (CH) has been extensively used in the food industry as food packaging material, especially in edible films and coatings (Tual, Espuche, Escoubes, & Domard, 2000). Furthermore, it has been reported that chitosan has a number of functional properties including antioxidant and antimicrobial properties, and chitosan films may serve as oxygen barriers (Jeon, Kamil, & Shahidi, 2002). Chitosan can also offer protection from free radicals with antioxidant activity that varies with its molecular weight and viscosity (Harish Prashanth & Tharanathan, 2007). However, chitosan has poor solubility in physiological solvents due to its strong

☆ Approved for publication by the director of the Louisiana Agricultural Experimental Station as Manuscript number 2013 237-9646.

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http://dx.doi.org/10.1016/j.lwt.2013.12.033

intermolecular hydrogen bonding, thereby greatly limiting its applications in the food industry.

Chitosan nanoparticles have been synthesized for use as drug delivery systems and gene carriers (Mao et al., 2001; Qi, Xu, Jiang, Hu, & Zou, 2004). Chitosan nanoparticles are conventionally prepared by an ionotropic gelation process of chitosan with tripolyphosphate anions (Harish Prashanth & Tharanathan, 2007). According to Pan et al. (2002) chitosan nanoparticles can improve the pharmacological bioavailability of bioactives in the human intestinal tract because of their greater ability to penetrate the epithelia than particles in the micrometer size range. Moreover, a higher antimicrobial activity of chitosan nanoparticles compared to conventional chitosan has been reported (Qi et al., 2004). The greater activity is due to the nanoparticles' small size and quantum size effect.

Considerable information about the applications of chitosan nanoparticles in the pharmaceutical area has been reported; however, information about the applications of chitosan nanoparticles in the food industry is rather limited. Thus, the aim of this study was to evaluate the potential of chitosan nanoparticles as a novel glazing material for shrimp frozen by cryogenic freezing.

2. Materials and methods

2.1. Materials

Fresh, extra-large size (57–66 units per kg) head-on white shrimp (*Litopenaeus setiferus*) were purchased from a local seafood store in Baton Rouge, LA. Shrimp were transported on ice to the Food Processing Pilot Plant, Louisiana State University Agricultural Center, where they were kept at 4 °C until use. Medium molecular weight (190–310 kDa) chitosan (CH), technical grade sodium tripolyphosphate (TPP) and all other analytical grade reagents were obtained from Sigma Aldrich (St. Louis, MO).

2.2. Preparation of glazing solution containing chitosan nanoparticles (CH–TPP)

Glazing solutions containing CH–TPP nanoparticles were prepared by modifying a method developed by Calvo, Remunan-Lopez, Vila-Jato, and Alonso (1997) based on the ionotropic gelation of CH with TPP anions. According to Fernández-Urrusuno, Calvo, Remuñán-López, Vila-Jato, and Alonso (1999), ionotropic gelation occurs when the negatively charged TPP interacts with the positively charged amino groups of CH. A solution of 1 (mL/100 mL) Acetic Acid (AA) was prepared by dissolving 10 mL of reagent-grade acetic acid in 990 mL of distilled water (DW). Then, two CH solutions (0.25 (g/100 mL) and 0.50 (g/100 mL)) were prepared by respectively adding 2.5 g and/or 5 g of CH to 1 L of AA, stirring 1 h at room temperature and sonicating with an ultrasonic processor (Model WU-04711-70, Cole-Parmer Inc., Vernon, IL, USA) fitted with a 22 mm tip diameter for 30 min in an ice bath at 4 °C. The resulting 0.25 (g/100 mL) (25CH) and 0.50 (g/100 mL) (50CH) CH solutions were transparent and odorless.

A 0.083 (g/100 mL) (25TPP) and a 0.167 (g/100 mL) (50TPP) TPP in AA solutions were prepared. CH–TPP nanoparticles were prepared by adding 0.83 g and 1.67 g of TPP to the previously prepared 25CH and 50CH solutions, respectively. Afterwards, the mixtures were sonicated for 30 min at room temperature and processed by an ultra-shearing device (OMNI, Ultrashear M, Omni International, Kennesaw, GA) for 30 min at 25,000 rpm. Two solutions containing CH–TPP nanoparticles were prepared: 1) a mixture made with 0.25 (g/100 mL) CH and 0.083 (g/100 mL) TPP (25CH–TPP) and 2) a mixture made with 0.50 (g/100 mL) CH and 0.167 (g/100 mL) TPP (50CH–TPP). According Gan, Wang, Cochrane, and McCarron (2005), CH–TPP nanoparticles are spontaneously formed via the TPP initiated ionotropic gelation process; and a CH to TPP weight ratio of 3:1 was used based on the results reported in the same study.

2.2.1. Characterization of chitosan nanoparticles

Particle size and size distribution (polydispersion index, PdI) of CH–TPP nanoparticles were determined by dynamic light scattering (DLS) using a Malvern Zetasizer Nano ZS (Malvern Instruments Ltd., Worcestershire, U.K.). Zeta potential measurements were carried out with the same Malvern Zetasizer Nano ZS equipment. A transmission electron microscopy (TEM) was performed using a JEOL 100-CX (JEOL USA Inc., Peabody, MA) instrument operated at 200 kV. Approximately 1 μL of the solution containing CH–TPP nanoparticles was pipetted onto a copper grid (the grid hole size is 45 μm) with carbon film. The solution was allowed to air-dry and settle for one minute prior to removing the excess liquid with filter paper. The loaded grid was placed into the sample holder of the TEM after filling with liquid nitrogen.

2.3. Proximate analysis of shrimp

Shrimp were manually de-headed and de-shelled. Then, the shrimp were analyzed for moisture, protein, lipid, and ash content. Moisture content was determined according to the AOAC official method 930.15 (AOAC, 1999). Crude protein was determined by following the AOAC official method 992.15 (AOAC, 2006) using Perkin Elmer Nitrogen Analyzer (Model 2410, Perking Elmer Instruments, Norwalk, CT). The crude protein (g/100 g) was reported as 6.25 times the nitrogen content. Lipid content was determined by following the method established by Bligh and Dyer (1959). Ash content was determined according to the AOAC official method 942.05 (AOAC, 1999). All of the determinations were carried out in triplicate.

2.4. Freezing of shrimp

The de-headed and de-shelled shrimp were frozen using a cabinet-type cryogenic freezer with liquid nitrogen (Air Liquide, Houston, TX, USA). Thermocouples were connected to a data logger (Comark®, Comark Ltd. Stevenage, Herts, UK) to monitor the temperature changes during cryogenic freezing. The thermocouples were inserted at the center of the second abdominal segment of the shrimp and the freezing was carried out until the shrimp temperature reached −21 °C.

2.5. Glazing of shrimp

The cryogenically frozen shrimp were glazed at the Food Processing Pilot Plant, Louisiana State University Agricultural Center. The frozen shrimp were glazed with distilled water (DWG); 0.25 (g/100 mL) chitosan solution (25CH); 0.50 (g/100 mL) chitosan solution (50CH); 0.083 (g/100 mL) TPP (25TPP); 0.167 (g/100 mL) TPP (50TPP); 1 (mL/100 mL) acetic acid (ACG); CH–TPP nanoparticles made with 0.25 (g/100 mL) CH + 0.083 (g/100 mL) TPP (25CH–TPP); and/or CH–TPP nanoparticles made with 0.50 (g/100 mL) CH + 0.167 (g/100 mL) TPP (50CH–TPP). Hundred grams batches of shrimp were glazed by dipping each batch in the appropriate glazing solution at room temperature for 30 s and then allowing them to drip for 5 s before packing in Zip Lock® bags. The shrimp were weighed before and after glazing and stored at −21 °C in a blast freezer for 30 d. Quality analysis was performed after 1, 3, 5, 20 and 30 days of frozen storage.