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Carbohydrate Polymers 69 (2007) 707–712

Carbohydrate Polymers

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Physical characteristics of decolorized chitosan as affected by sun drying during chitosan preparation

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Received 22 May 2006; received in revised form 7 February 2007; accepted 10 February 2007
Available online 16 February 2007

Abstract

Some physical characteristics of decolorized chitosan as affected by sun drying, which was used to replace a bleaching step during chitosan preparation, were evaluated. One bleached and four unbleached chitosans were prepared and dried for 4 h by heat treatment at 60 °C or sun drying. The moisture content of chitosans dried by heat treatment was lower than that of chitosans dried by sun drying. Decoloration of the chitosan could be achieved more effectively by sun drying after deacetylation than by using a bleaching agent in the chitin preparation. Use of a bleaching agent significantly reduced the viscosity of the chitosan solution. A sequence of heat drying and sun drying in chitin and chitosan production (without using a bleaching agent) generally produced a whiter chitosan with higher viscosity without affecting water- and fat-binding capacities, compared to the bleached chitosan.

Keywords: Chitosan; Decoloration; Physical properties; Sun drying; Viscosity

1. Introduction

Chitosan is a natural biopolymer derived by deacetylation of chitin, a major component of the shells of crustacean such as crab, shrimp, and crawfish. During the past several decades, chitosan has been receiving increased attention for its commercial applications in biomedical, food, and chemical industries (Sandford & Hutchings, 1987). Chitosan is now widely produced commercially from crab and shrimp shell wastes with a molecular weight (M_w) usually in the range of 10^5–10^6 Da and viscosity reaching or exceeding 1500 cP (No & Meyers, 1995; Sugano, Yoshida, Hashimoto, Enomoto, & Hirano, 1992; Van Ornum, 1992).

The typical production of chitosan from crustacean shell generally consists of four basic steps: demineralization (DM), deproteinization (DP), decoloration (DC), and deacetylation (DA) (No & Meyers, 1995); this process is costly, thus limiting wider applications of chitosans. Simplification of chitosan production by elimination of the DC step would considerably reduce production cost due to reduction in chemical usage, process time, and voluminous wastewater discharge.

In chitin production, the DM and DP steps produce a colored chitin product. When a bleached chitinous product is desired, pigments can be removed with reagents such as ethanol and ether (Hackman, 1954), sodium hypochlorite solution (Blumberg, Southall, Van Rensburg, & Volckman, 1951; No, Meyers, & Lee, 1989), absolute acetone (Kamasastri & Prabhu, 1961; Mima, Miya, Iwamoto, & Yoshikawa, 1983), chloroform (Anderson, de Pablo, & Romo, 1978), hydrogen peroxide (Brine & Austin, 1981; Moorjani, Achutha, & Khasim, 1975), or ethyl acetate (Brzeski, 1982). In general, the organic solvents are not as effective as the bleaching agents such as sodium hypochlorite or hydrogen peroxide in removing pigments from crab or crawfish shell (No et al., 1989; No & Lee, 1995). As bleaching agents considerably reduce the viscosity of the chitosan product, Moorjani et al. (1975) recommended that it is not desirable to bleach the material at any stage. Therefore, an alterna-

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doi:10.1016/j.carbpol.2007.02.007

tive, yet effective and economical decoloration method that will yield decolorized chitosan with high viscosity should be developed.

Once high-viscosity chitosan is prepared, low-viscosity chitosan, if necessary, can be subsequently obtained by chemical or enzymatic hydrolysis (No, Nah, & Meyers, 2003). The functional properties of chitosan are reported to be dependent on its molecular weight or viscosity (No & Meyers, 1995). Earlier investigations demonstrated that chitosans with higher molecular weight (or viscosity) were more effective as food preservatives than those with lower molecular weight in extending the shelf-life of bread (Lee et al., 2002), pork (Lee, Park, & Ahn, 2003), sausage (Youn, Park, & Ahn, 2000), and fish (Jeon, Kamil, & Shahidi, 2002). Furthermore, some studies reported that chitosan was more effective in inhibiting growth of bacterial than were chitosan oligomers (No, Park, Lee, & Meyers, 2002; Uchida, Izume, & Ohtakara, 1989).

The objectives of the present research were to prepare decolorized chitosan with high viscosity by sun drying without using a bleaching agent, and to characterize some physical properties of these chitosan products.

2. Materials and methods

2.1. Materials

Dried crab (*Chionoecetes opilio*) leg shell was obtained from Keumho Chemical (Seoul, Korea). The shell was ground through a Wiley mill (model 4, Thomas Scientific, Swedesboro, NJ, USA) with a 2-mm mesh screen and subsequently sifted with 20 (0.841 mm) and 40 mesh (0.425 mm) sieves using a portable sieve shaker (JISICO, Seoul, Korea). The ground shell with 0.841–0.425 mm particle size was used throughout this research to obtain reproducible and consistent results. Commercially available refined soybean oil was used for the fat-binding capacity study.

2.2. Production of chitosan

The production of chitosan involved the DM, DP, DC, and DA steps (No, Lee, Park, & Meyers, 2003). The ground crab leg shell was demineralized with 1 N HCl for 30 min at ambient temperature with a solid/solvent ratio of 1:15 (w/v). Following the DM step, the demineralized shell was collected on a 100-mesh sieve, washed to neutrality in running tap water, rinsed with deionized water, and filtered to remove excess moisture. The DP step was accomplished by treating the demineralized shell with 3% NaOH for 15 min at 15 psi/121 °C and a solid/solvent ratio of 1:10 (w/v). The residue was then washed and filtered as mentioned above. For the DC step, the resulting chitin residue was bleached with 10% sodium hypochlorite solution for 5 min with a solid/solvent ratio of 1:10 (w/v). The unbleached or bleached chitin was collected, washed as mentioned above, and dried at 60 °C for 4 h in a forced-air oven or by sun drying (approximately at 23 °C) for 4 h.

Table 1
Preparation of chitosans under various decoloration and drying conditions

Chitosan	Chitosan production process[a]					
	DM[b]	DP[b]	DC[b]	Drying	DA[b]	Drying
CH 1	○[c]	○	○	60 °C, 4 h	○	60 °C, 4 h
CH 2	○	○	×[c]	60 °C, 4 h	○	60 °C, 4 h
CH 3	○	○	×	60 °C, 4 h	○	Sun, 4 h
CH 4	○	○	×	Sun, 4 h	○	60 °C, 4 h
CH 5	○	○	×	Sun, 4 h	○	Sun, 4 h

[a] Sequentially from left to right.

[b] DM, demineralization; DP, deproteinization; DC, decoloration; DA, deacetylation.

[c] ○, conducted; ×, not conducted.

The DA step was achieved by treating chitin under conditions of 15 psi/121 °C with 45% NaOH for 30 min and a solid/solvent ratio of 1:10 (w/v). The resulting chitosan was collected, washed as mentioned above, and dried at 60 °C for 4 h in a forced-air oven or by sun drying (approximately at 23 °C) for 4 h. Five chitosans, designated as CH1, CH2, CH3, CH4, and CH5, were prepared under various decoloration and drying conditions (Table 1).

2.3. Measurement of moisture, viscosity, and color

The moisture content was determined using a halogen moisture analyzer (HG53, Mettler Toledo, Greifensee, Switzerland). Viscosity was determined with a Brookfield viscometer, model LVDV-II+ (Brookfield Engineering Labs., Stoughton, MA, USA). Chitosan solution was prepared in 1% (v/v) acetic acid at a 0.5% (w/v) concentration on a moisture-free basis. Viscosity measurements were made using a small sample adapter in the solution (8 mL) at 25 ± 0.3 °C, and reported in centipoise (cP). Color measurements were measured with a portable Minolta Chroma Meter CR-200 (Minolta Camera Co., Ltd, Osaka, Japan) using illuminant C, and reported as L^* (lightness), a^* (+ for redness and − for greenness), and b^* (yellowness). Three measurements were made at different locations on each sample.

2.4. Water- and fat-binding capacities

Water-binding capacity (WBC) and fat-binding capacity (FBC) of chitosan were measured using a modified method of Wang and Kinsella (1976). Water or fat absorption was initially carried out by weighing a centrifuge tube (50 mL) containing 0.5 g of sample, adding 10 mL of water or soybean oil, and mixing on a vortex mixer for 1 min to disperse the sample. The contents were left at ambient temperature for 30 min with shaking for 5 s every 10 min and centrifuged at 3200 rpm for 25 min. After the supernatant was decanted, the tube was weighed again. WBC and FBC were calculated as follows: WBC (%) = [water bound (g)/sample weight (g)] × 100; FBC (%) = [fat bound (g)/sample weight (g)] × 100.

2.5. Statistical analysis

All experiments were carried out in triplicate, and means ± standard deviations were reported. Means of the main effects were separated by Duncan's multiple-range test using the SPSS (Statistical Package for Social Sciences, SPSS Inc., Chicago, IL) software package.

3. Results and discussion

3.1. Moisture content

Fig. 1 shows moisture contents of five chitosans (CH 1–5), ranging from 2.60% to 7.27%. After deacetylation, the moisture content (2.60–3.41%) of chitosans (CH 1, CH 2, and CH 4) dried by heat treatment at 60 °C for 4 h was lower than that (6.41–7.27%) of chitosans (CH 3 and CH 5) dried by sun drying.

According to KFDA (1995), the moisture content of chitosan powder should be below 10%. The moisture content of five chitosans in our present study was all less than 8%. In our preliminary study conducted during September, we found that sun drying more than 4 h did not further noticeably decrease the moisture content of chitosan. However, the moisture content of chitosan will vary depending on the season, relative humidity, and intensity of sun light.

3.2. Color

Color L^*, a^*, and b^* values of five chitosans are shown in Fig. 2. Among five chitosans, the highest L^* value and the lowest a^* and b^* values were observed for CH 3, followed by CH 5; both chitosans were dried by sun light after the DA step. This suggests that, under specific chitosan production conditions used in this study, drying by sun light yielded whiter, less red, and less yellow chitosan, compared with drying by the forced-air oven. There were slight differences in color values among the other three chitosans (CH 1, CH 2, and CH 4), except for CH 2 with a considerably higher a^* value. The reported color of chitosans in the literature ranges from white to tan (No & Meyers, 1995). According to visual observation, CH 3 was brighter or whiter than CH 5, CH 1 and CH 4 were lightly brown, while CH 2 was lightly pink.

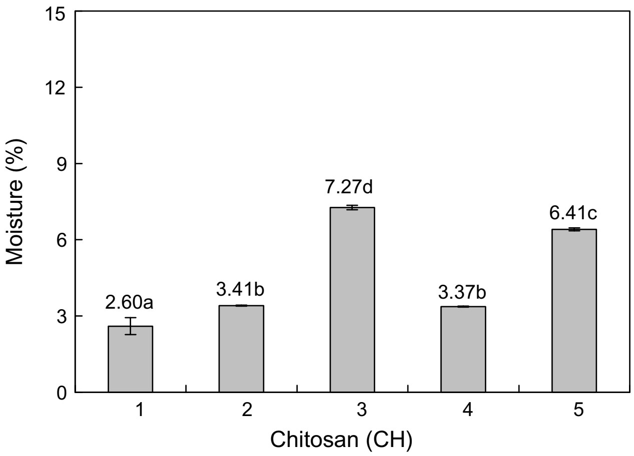

Fig. 1. Moisture content of chitosans prepared under various decoloration and drying conditions. Bars/mean values with different letters are significantly different ($p < 0.05$). See Table 1 for chitosan and process description.

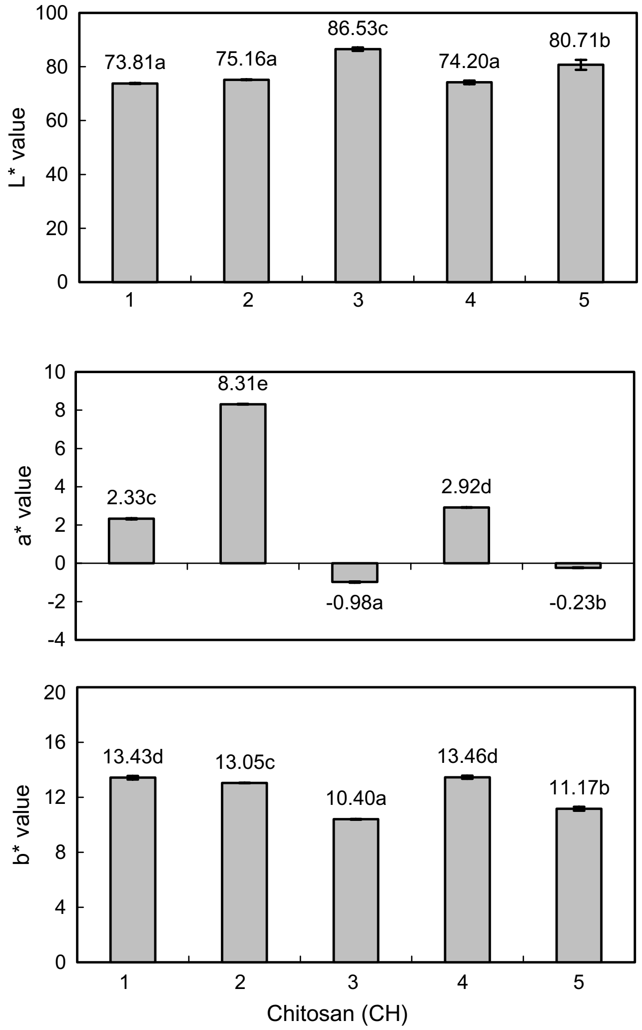

Fig. 2. Color L^*, a^*, and b^* values of chitosans prepared under various decoloration and drying conditions. Bars/mean values with different letters are significantly different ($p < 0.05$). See Table 1 for chitosan and process description.

Data from Fig. 2 indicate that decoloration of the chitosan (CH 3 and CH 5) could be achieved more effectively by sun drying after deacetylation than by using a bleaching agent in the chitin preparation as observed for CH 1. The main component of carotenoid fraction in crustacean exoskeleton is astaxanthin (No et al., 1989). The oxidative degradation of carbon–carbon double bonds caused decoloration of carotenoids (Henry et al., 2000). Therefore, decoloration of chitosan (CH 3 and CH 5) was likely due to the oxidative destruction of double bonds present in astaxanthin by UV light from the sun drying step. From a preliminary study in our laboratory, we found that pigments remaining in chitosan were completely bleached within 5 min by irradiation with UV light (data not shown).

Decoloration by a bleaching agent or by sun drying in the chitin preparation initially produced white or light-pink chitins that were subsequently converted into light-brown chitosans (CH 1 and CH 4) after the DA step. The light-brown color of chitosan may have been due to browning of alkali solution used after the DA step rather than by degradation of pigments present in the chitin during the DA step (Anderson et al., 1978). Production of decolorized chitosan by sun drying without using a bleaching agent would considerably reduce production cost due to reduction in chemical usage, process time, and voluminous wastewater discharge.

3.3. Viscosity

The viscosity values of five chitosan solutions at 0.5% (w/v) concentration are shown in Fig. 3. Decoloration of chitin with a bleaching agent significantly reduced the viscosity (34 cP) of the CH 1 solution, which was much lower than that (295–661 cP) of the unbleached chitosan (CH 2–5) solutions. Similarly, Nadarajah, Prinyawiwatkul, No, Sathivel, and Xu (2006) observed that bleaching with acetone followed by sodium hypochlorite solution considerably reduced the viscosity (35 cP) of the final chitosan solution compared with that (1164 cP) of the unbleached chitosan solution. Among CH 2–5, the highest viscosity was observed in solution of CH 2, followed by CH 4, CH 3, and CH 5. This indicates that chitosan with higher viscosity can be obtained by heat drying (CH 2 and CH 4) rather than by sun drying (CH 3 and CH 5) after the DA step. However, the former two chitosans showed lower L^* value and higher a^* and b^* values than the latter two chitosans (Fig. 2). In general, a bleached chitosan product is required in commercial application. In view of color and viscosity, CH 3 is therefore more desirable than CH 5; the former having higher viscosity and brighter or whiter color than the latter.

Data from Figs. 2 and 3 clearly indicate that a white chitosan product with high viscosity (CH 3) can be simply produced by sun drying after the DA step without using a bleaching agent. The viscosity (424 cP) of CH 3 solution was 12.5 times higher than that (34 cP) of CH 1 solution. The viscosity of CH 3 solution observed in this study was also higher than those (26–360 cP) of six commercial chitosan solutions at a 1.0% (w/v) concentration reported by No, Lee, and Meyers (2000). However, the reported viscosity of chitosan solutions, all dissolved in acetic acid, varied considerably from 60 to 5110 cP (No & Meyers, 1995).

3.4. Water- and fat-binding capacity

The functional properties of chitosan differ with preparation methods. Thus, the relationship between the process conditions and the functional properties of chitosan products should be monitored. Water-binding capacity (WBC) and fat-binding capacity (FBC) of chitosans are shown in Figs. 4 and 5.

The WBC values of chitosans were similar ranging from 523% to 539%, except for that of CH 5 (593%) (Fig. 4). Similarly, no significant differences in FBC (433–477%) were observed among chitosans, except for CH 2 (394%) (Fig. 5). Sun drying (CH 5) or heat drying (CH 2) applied in both chitin and chitosan preparation resulted in increased WBC and decreased FBC, respectively, compared with other four chitosans. It is noteworthy to mention that sun drying after the DA step produced a whiter chitosan with higher viscosity (CH 3) without affecting WBC and FBC functionality compared to CH 1 prepared under the typical chitosan production condition.

Cho, No, and Meyers (1998) and No et al. (2000) reported that WBC and FBC differed among commercial

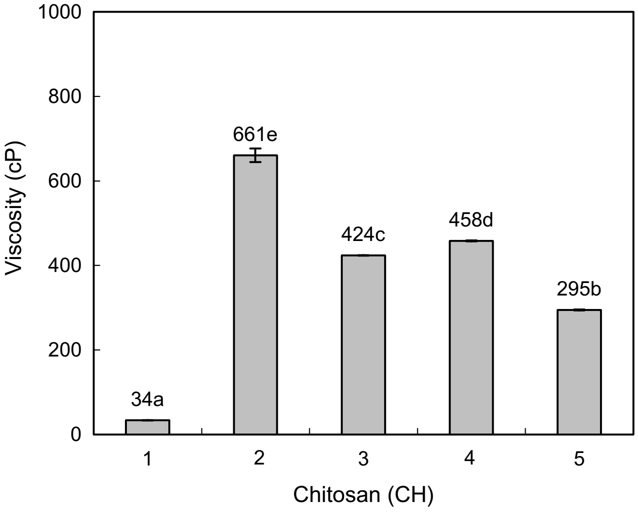

Fig. 3. Viscosity of 0.5% w/v chitosan solutions (in 1% v/v acetic acid) prepared under various decoloration and drying conditions. Bars/mean values with different letters are significantly different ($p < 0.05$). See Table 1 for chitosan and process description.

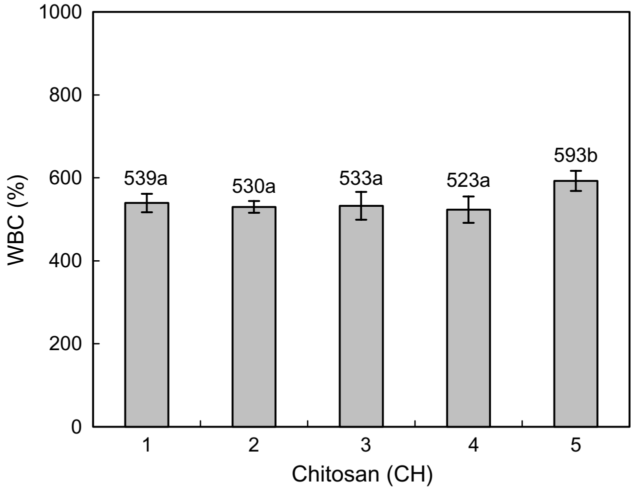

Fig. 4. Water-binding capacity (WBC) of chitosans prepared under various decoloration and drying conditions. Bars/mean values with different letters are significantly different ($p < 0.05$). See Table 1 for chitosan and process description.

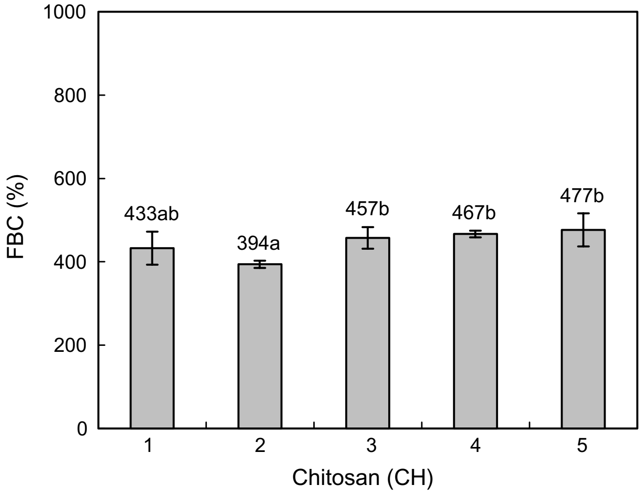

Fig. 5. Fat-binding capacity (FBC) of chitosans prepared under various decoloration and drying conditions. Bars/mean values with different letters are significantly different ($p < 0.05$). See Table 1 for chitosan and process description.

chitosans. According to Cho et al. (1998), WBC and FBC of five commercial chitosan products ranged from 458% to 805% and 314% to 535%, respectively. WBC and FBC of six commercial chitosan products observed by No et al. (2000) were in the range of 355–611% and 217–403%, respectively. The WBC (523–593%) and FBC (394–477%) of chitosans observed in this study were comparable to those of commercial chitosans reported by Cho et al. (1998) and No et al. (2000).

4. Conclusion

This study demonstrated that decolorized chitosan with high viscosity could be prepared with the aid of sun drying without using a bleaching agent. Particularly, heat drying and sun drying applied in the chitin and chitosan production, respectively, produced a chitosan (CH 3) with desirable white color and high viscosity, without affecting WBC and FBC functionality compared to the bleached chitosans. Use of a bleaching agent caused significantly reduced viscosity of chitosan in addition to the observed undesirable light brown color. Sun drying after deacetylation step was more effective in producing decolorized chitosan in contrast to heat drying. Production of white-colored chitosan with the aid of sun drying and without using a bleaching agent would considerably reduce production cost due to reduction in chemical usage, process time, and voluminous wastewater discharge. However, further studies are needed to maximize such effectiveness of sun drying due to variation in season and weather conditions.

Acknowledgement

This work was partly supported by the Regional Research Center (RRC) program of Ministry of Commerce, Industry and Energy (MOCIE).

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