RADIATION DEGRADATION OF CHITOSAN

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Abstract

In order to obtain an oligochitosan, degradation of chitosans were carried out in solid state and liquid state. The effects of an irradiation on the molecular weight and viscosity of the chitosan were investigated using Ubbelohde Capillary Viscometer and Brookfield Viscometer respectively. The molecular weight and viscosity of the chitosans decreased with an increase in the irradiation dose. In the presence of hydrogen peroxide, the molecular weight of chitosan can be further decreased.

Abstrak

Untuk menghasilkan oligokitosan, proses degradasi ke atas kitosan dijalankan dalam keadaan pepejal atau cecair. Kesan radiasi ke atas berat molekul dan kelikatan dikajo menggunakan Ubbelohde Capillary Viscometer and Brookfield Viscometer. Berat molekul dan kelikatan kitosan menurun dengan peningkatan dos sinaran. Dengan penambahan hydrogen peroxide, berat molekul kitosan didapati semakin rendah

Keywords : Oligochitosan, low molecular weight, viscosity, radiation processing

INTRODUCTION

Chitosan is a cationic polymer, which is the second most abundant polymer in nature after cellulose. Chitosan is a linear co polymer polysaccharide consisting of β (1–4)-linked 2-amino-2-deoxy-D-glucose (D-glucosamine) and 2-acetamido-2-deoxy-D-glucose (N-acetyl-D-glucosamine) units. The term chitosan is used to describe a series of polymers of different degrees of deacetylation (DD), defined in terms of the percentage of primary amino groups in the polymer backbone, and average molecular weights (Mw). Chitosan has found applications in many primary industries such as: agriculture, paper, textiles, pharmacology, cosmetology and wastewater treatment (Berger et al. 2004; Lloyd et el., 1998). However, in some fields (especially in medicine and the food industry) the application of this polysaccharide is limited by its high molecular weight resulting in its low solubility in aqueous media (Minagawa et al. 2007; Biskup et al. 2005). Low-molecular weight chitosan can be prepared by chemical (Hasegawa et al. 1993), enzymatic (Ilyina et al. 2000) or radiation (Won-Seok et al. 2002) degradation of high molecular weight polymer.

Radiation has been found as one of the most popular tools for modification of polysaccharides. Without using any chemicals or high temperature treatment, radiation is known for its safer, environmental friendly and easier method to modify polymers. Numbers of studies have been done on radiation degradation of natural polymer such as chitosan, carrageenan (Abad et al., 2009) and sodium alginate. Unfortunately, the reduction in molecular weight must be done in higher dose in order to get lower molecular weight. Studies have been carried out using hydrogen peroxide (H_2O_2), a powerful oxidizing species, in degradation of chitosan. However, it gave some drawback as it can change the colour of the final product and chemical structure of chitosan as reported by Qin and friends (2002). The changes such as formation of carboxyl groups and deamination increased with the decrease of Mw. Combined chemical-radiation method can also be used to produce oligo polysaccharide. Attempt on chitosan dissolved in various percentage of H_2O_2 before subjecting the chitosans to gamma radiation revealed that the molecular weight decreased effectively than that of chitosan irradiated without H_2O_2 (Yi Hong et al. 2004).

In this paper, we propose a method to produce chitosan oligomer effectively and study the effect of gamma irradiation on chitosan dissolved in lactic acid and in the presence of hydrogen peroxide.

EXPERIMENTAL

Materials

Chitosan powder was purchased from China with the following properties, 90.6% of DDA, 10% water content. Gamma irradiation was used throughout of this study for the production of oligochitosan. Hydrogen peroxide, H_2O_2, was purchased from Sigma and lactic acid was obtained from OFT Chemicals Sdn. Bhd. All reagents were used as received without any purification.

Preparation of oligochitosan

Chitosan powder was irradiated in plastic bags with gamma radiation using Sinagama Facility within the dose range of 25–100 kGy. The irradiated chitosan were then dissolved in lactic acid prior to irradiation using gamma irradiation at 12 kGy combined with a small amount of hydrogen peroxide.

Molecular Weight Determination

Molecular weight was identified by viscometric measurements using an Ubbelohde Capillary Viscometer type 531/10 I. Average molecular weights were calculated from $[\eta] = KM^{\alpha}$ equation, where $K = 1.4 \times 10^{-2}$ (dm^3/g) and a = 0.83 determined in 0.25M Sodium Acetate and 0.25M Acetic Acid solution at 25°C. The solution was prepared 24 hours before doing the measurement and can only be used within 24 hours.

Viscosity Measurement

Viscosity was measured using spindle type viscometer model Brookfield DV II+ at 25°C. The viscosity of chitosan was measured directly after dissolving the unirradiated and irradiated chitosan in lactic acid.

RESULT AND DISCUSSION

Changes in Molecular Weight and Viscosity

Upon radiation, two main reactions which influence the final properties of polymer: a) scission of main chain, also known as degradation and b) cross-linking, the opposite process to degradation. The former will be followed by reduction in molecular weight while the later will cause an increase in molecular weight. Degradation process usually occurs when natural polymer is subjected to ionizing radiation. Degradation rate of polysaccharide depends on many factors such as types of ionizing source and condition of the sample. Reduction of molecular weight was found to be lower when the sample was irradiated in liquid state (Fumio Yoshii, 2004).

Figure 1 illustrated effect of radiation on chitosan in powder form after exposing under gamma radiation with various doses up to 100kGy. The most pronounced decrease was at lower dose up to 50kGy and after that, the reduction in molecular weight was not very significant. At dose 50kGy the molecular weight drop from 218 269Da to 36 564Da. This reduction was due to chain scission of chitosan backbone, where degradation process took place. A reduction of molecular weight was followed by decreasing in viscosity of chitosan. Changes of viscosity of chitosan with irradiation dose are depicted in figure 1. A sudden drop of viscosity was observed at 25kGy where the viscosity reduce from 1 396cPs to 98cPs. After 50kGy, viscosity of chitosan was remained. These data suggest that the optimum radiation dose for chitosan powder was 50kGy.

Effect of Hydrogen Peroxide

A reduction of molecular weight can be further decreased by adding hydrogen peroxide, H_2O_2 as shown in figure 2. The irradiated powder chitosan were then irradiated at 12kGy in a presence of small amount of H_2O_2. A marked drop of molecular weight was observed for irradiated powder chitosan at dose 25kGy where the molecular weight reduced to 12 684Da. It is obvious that with combination of gamma irradiation and hydrogen peroxide in liquid state, the decrease in molecular weight was higher compared to chitosan which irradiated using gamma irradiation alone. Under gamma irradiation in liquid state in the presence of H_2O_2, the primary reactions might occur as follows :

$$H_2O \rightarrow e_{aq}^-, OH\bullet, H\bullet, H_2O_2, H_2, H^+, OH^-, H_3O^+$$
$$H\bullet + H_2O_2 \rightarrow H_2O + \bullet OH$$
$$e_{aq}^- + H_2O_2 \rightarrow \bullet OH \rightarrow OH^-$$
$$H_2O_2 \rightarrow 2 \bullet OH$$
$$R + \bullet OH \rightarrow \bullet R + H2O$$
$$R + \bullet H \rightarrow \bullet R + H_2$$
$$\bullet R \rightarrow R_1 + R2$$

OH radical is a much more powerful oxidant. This radical which was derived from the radiolysis of water and H_2O_2 will break the chitosan backbone and led to a smaller chain. Thus, the addition of hydrogen peroxide can further decrease the molecular weight of chitosan. Tian and friends (2004) reported H_2O_2 even in a small quantity gradually reduces molecular weight of chitosan.The same phenomenon was found in viscosity observation when chitosan irradiated in liquid state in the presence of H_2O_2.

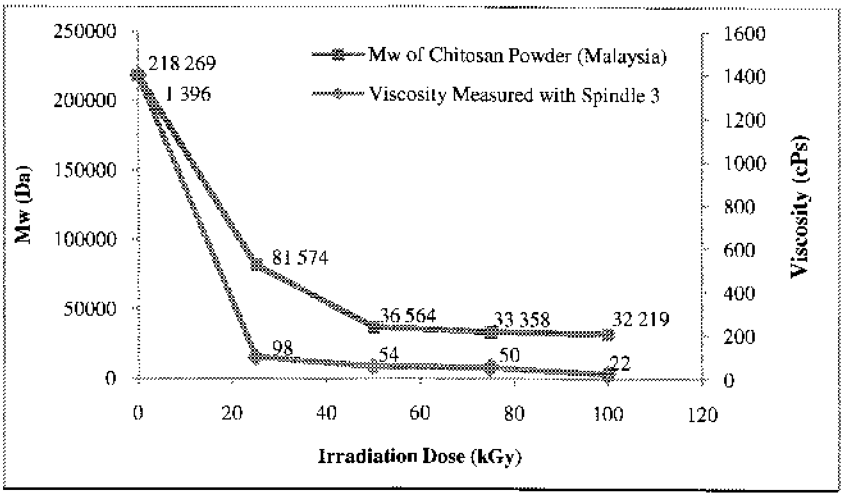

Figure 1: Changes of molecular weight and viscosity as function of irradiation dose. Chitosan was irradiated in powder form using gamma radiation at 25, 50, 75 and 100kGy.

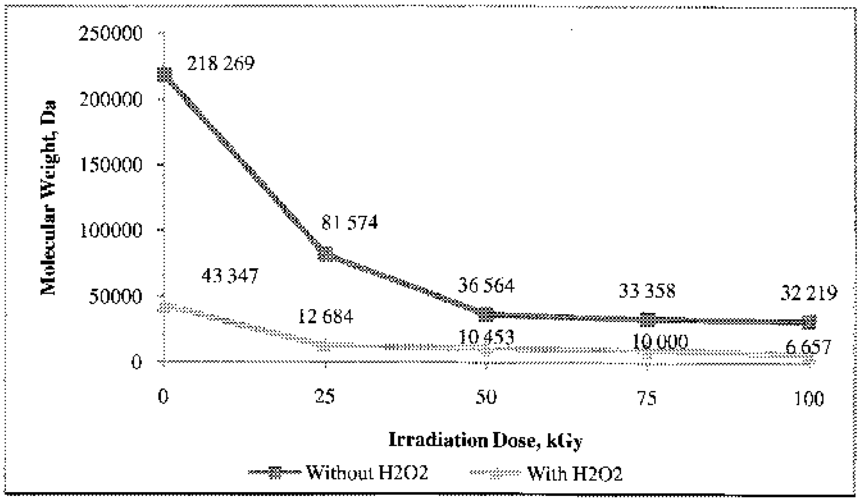

Figure 2: Effect of hydrogen peroxide on molecular weight of chitosan

Effect of irradiation on colour changes

Radiation not only affected the molecular weight, it is also gave some effect on colour changes. Figure 3 shows colour change of non-irradiated and irradiated chitosan in powder form with doses 25, 50, 75 and 100kGy. The colour of irradiated chitosan changed to a more intense brown with increasing irradiation dose.

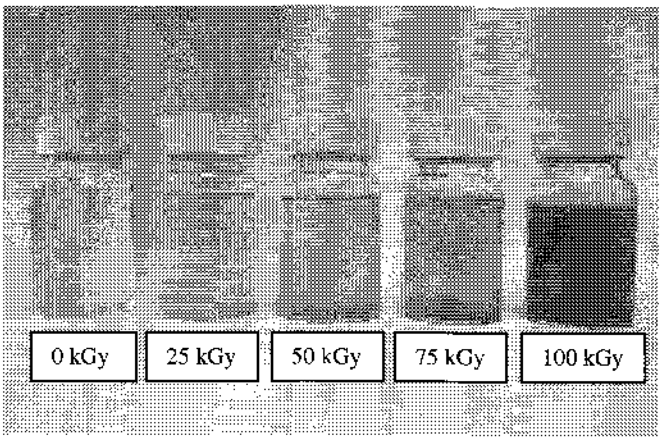

Figure 3: Colour changes in chitosan after exposing under gamma radiation at various doses.

CONCLUSION

Radiation technology has been proven as a method that can be used to reduce the molecular weight of chitosan and other natural polymer. The radiation treatment on chitosan in the presence of hydrogen peroxide could reduce its molecular weight very effectively. Molecular weight of chitosan was found to decrease from 218 000 Da to 36 654 when chitosan was irradiated at dose 50kGy by gamma radiation while in the presence of H_2O_2 in liquid state, the molecular weight can be degraded up to 10 453Da.

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