Facile Method to Manipulate the Molecular Weight and Practical Mass Production of Chitosan by Mechanical Shearing and Concurrent Ultrafiltration Treatment

Min Lang Tsai,[1] Lan Zang Tseng,[1] Hsiang Wei Chang,[1] Chu Hsi Hsu,[1,2] Rong Huei Chen[1]

[1]*Department of Food Science, National Taiwan Ocean University, Keelung 20224, Taiwan*
[2]*Department of Food and Beverage Management, Yuanpei University, Hsinchu 30015, Taiwan*

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ABSTRACT: The objective of this study was to propose a facile method to manipulate the molecular weight and practical mass production of chitosan by mechanical shearing and concurrent ultrafiltration (UF) treatment. The proposed method was based on the degradation rate and rate constant of various process variables, such as: solution temperature, reaction time, concentration of chitosan solution, with or without concurrent removal of degraded fragments during mechanical shearing. The result obtained was that the degradation rate constant was 1.8–6.0 times higher for those using UF to remove smaller degraded molecules concurrently during treatment, than that without UF treatment. The degradation rate constant increased with increasing solution temperature; however, the solution temperature should not exceed than 50°C to prevent the undesired color changes of the resulting product. A method combining mechanical shearing/UF treatment at 50°C and ultrasonic radiation or microfluidization/UF treatment at 30°C is proposed here for a facile method to manipulate the molecular weight of the resultant chitosan with an energy saving, efficient and practical mass production. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 1442–1449, 2010

Key words: chitosan; mechanical shearing degradation; ultrafiltration; kinetics

INTRODUCTION

Chitin is composed of a larger proportion of *N*-acetyl-glucosamine and smaller portion of glucosamine by β-1, 4 glycoside into a high molecular weight biopolymer. It has a structure similar to that of cellulose. Chitosan, the most important derivate of chitin, is prepared by alkali deacetylation. Chitinous materials are considered to be the most widespread polycationic biopolymer, having huge resources, as well as nontoxic, biodegradable characteristics. Chitinous materials can be applied in food processing, agriculture, biomedicine, biochemistry, wastewater treatment, membranes, microcapsules, nanoparticles, and liquid crystalline material, etc.[1–5]

The molecular weight of chitinous materials is a very important parameter which affects their properties, such as viscosity and conformation of molecule,[6] physical characteristics of the chitosan capsules,[7] nanoparticle size,[5,8] and binding capacity with protein and DNA.[9] Therefore, it is important to develop a facile method, to manipulate the molecular weight while preserving their integrated structure, that is scaleable to mass production. Degradation methods currently used are: chemical methods,[10] enzymatic methods,[11] physical methods,[12–20] and microbial methods.[21] It is difficult to manipulate the molecular weights of the resultant chitosan via chemical methods. Enzymatic and microbial methods are not feasible for use in mass production. Whereas the ultrasonic method is an efficient mechanical method, the eroded metal ions of horn might contaminate the products. The mechanical shearing method has the advantages of: low cost, ease of access, ease of operation, and apparently, suitability regarding mass production with relative efficiency. Our proposed method is potentially quite promising.

The mechanism of the polymer shearing degradation proposed is such that during the high rate of shearing, the strong elongated flow encountered by the polymer may bring sufficient energy to disrupt the molecules.[22] Besides, the polymer sheared along the direction of shearing flow, Casale and Porter[23] reported that the entangled molecules facilitated the degradation reaction during the shearing treatment; therefore, the length of the polymer has

Correspondence to: R. H. Chen (rhchen@mail.ntou.edu.tw).

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to be long enough to be entangled and stretched by the shear force.[5]

Muzzarelli[24] reported that mechanical shearing can be used to prepare special molecular weight chitosan, and the molecular weight distribution range is narrowed. Austin et al.[25] employed mechanical shearing and a chemical method to prepare microcrystalline chitin. Chen et al.[13] reported that chitosan was degraded by mechanical shearing at different shear rates, reaction temperatures, chitosan concentration, and shear time; polydispersity was narrowed. Tsai et al.[5] compared different modes and input-energy levels of ultrasonic radiation and mechanical shearing on the changes in the mean diameter of resultant ionotropic gelation chitosan-sodium tripolyphosphate nanoparticles. The aim was to elucidate the different effects on the size and polydispersity differences caused by the cavitation effects versus stretch effects, resulting from the usage of different modes of mechanical energy.

The 84% degree of deacetylation (DD) chitosan were degraded by ultrasonic radiation and microfulidization, respectively, with or without concurrent ultrafiltration (UF) treatment to remove the small degraded fragments. The rate constants were 1.0–2.0 times for ultrasonic radiation and 1.3–1.6 times for microfluidization, respectively, with rates higher for those using concurrent UF treatment to remove small degraded fragments during ultrasonic operation and microfluidization than those not using UF ones.[18,26] UF membrane was reported to be a specific separation of the chitosan oligomers (dimer, trimer, and tetramer) from each others. The cell configuration of membranes (EDUF) and the pH of the medium affected the possibility of separation of oligomers.[27] Electromigration rates of the chitosan oligomers were varied between 1.05 and 14.45% depending on the operating conditions (molecular weight cut-off (MWCO) of membrane and processing time).[28]

A color change from light to dark yellow in the chitosan samples was observed after exposure to steam, and the intensity of the color change increased with increased heating time.[29] The color darkening of the heated chitosan may be attributed to the Maillard reaction.[29,30] The Maillard reaction will consume the free amino group ($-NH_2$) and affect the functional properties of the resultant chitosan products. Zeng et al.[31] reported that the Maillard reaction was occurring in chitooligomer during storage. The time, temperature, pH, moisture, oxygen, and reductant all had effect on the browning of chitooligomers. They suggested that $-NH_2$, amide and $-OH$ groups in chitooligomer were involved in the browning reaction.

The objective of this study was to propose a facile method to manipulate the molecular weight and practical mass production of chitosan by mechanical shearing and concurrent ultrafiltration treatment. The proposed method was derived from the results of the effects of various process variables, such as: solution temperature, reaction time, concentration of chitosan solution, and with or without concurrent removal of degraded fragment during mechanical shearing, on the degradation rate and rate constant.

EXPERIMENTAL

Chitosan preparation

Chitin was prepared from shrimp (*Solenocera prominentis*) waste via a modified method of Stanley et al.[32] Ground shrimp waste was treated with 0.5*M* NaOH at ambient temperatures to hydrolyze the surface flesh. The alkali treated waste was washed till neutral, then dried and disintegrated to obtain powder. The powder was passed through sieves of 40–60 meshes. The flake-free powder was soaked in 2*M* HCl for 2 h to remove the minerals, until no more CO_2 was derived. The demineralized powder was soaked in 2*M* NaOH at 80°C to hydrolyze the protein, and then washed with water till neutral. The alkali-treated powder was soaked in 1% $KMnO_4$ at room temperature for 1 h to oxidize the astaxanthin. It was then soaked in 1% oxalic acid at 80°C for 1 h in order to neutralize the $KMnO_4$; it was then washed and dried to derive a white chitin powder. Chitin powder was alkali deacetylated (50% NaOH) at 140°C for 3 h to get about 80% DD chitosan; this was washed till neutral and dried at 50°C to obtain the final product.[33]

Degree of deacetylation measurement

Infrared spectrometry was used to determine the DD of the chitosans.[34] Chitosan powder was strained through a 200 mesh sieve and then mixed with KBr (1 : 100), and pressed into a pellet. The absorbance of amide I (1655 cm^{-1}) and of the hydroxyl band (3450 cm^{-1}) was measured using a Bio-Rad FTS-155 infrared spectrophotometer. The band of the hydroxyl group at 3450 cm^{-1} was used as an internal standard to correct for disc thickness and for differences in chitosan concentration in making the KBr disc. The percentage of the amine group's acetylation in a sample is given by $(A_{1655}/A_{3450}) \times 115$. Here, A_{1655}, A_{3450} are the absorbance at 1650 cm^{-1} and 3450 cm^{-1}, respectively. Every sample measurement was repeated three times; the DD of the chitosan used in this study was 84%.

Molecular weight determination

The size exclusion high performance liquid chromatography (SE-HPLC) method of Tsaih and Chen[35] was followed. A column (7.8 mm × 30 cm) packed

with TSK gel G4000 PW_{XL} and G5000 PW_{XL} (Tosoh, Tokyo, Japan) was used. The mobile phase consisted of 0.2*M* acetic acid/0.1*M* sodium acetate, and 0.008*M* sodium azide. A sample concentration of 0.1% (w/v) was loaded and eluted with a flow rate of 0.6 mL/min by an LDC Analytical ConstaMetric 3500 pump (Riviera Beach, FL). The elute peak was detected by an RI detector (Gilson, M132, Middleton, WI), and the data analyzed with Chem-Lab software (Scientific Information Service, Taipei, Taiwan). Chitosans with known molecular weight (determined by light scattering) were used as markers. The calibration curve of the elution volume and molecular weight was established. The weight average molecular weights of the samples were calculated from the calibration curve with the Chem-Lab software; every sample measurement was repeated three times.

Color measurement

The 0.8% chitosan solutions were mechanically sheared with a homogenizer (Polytrom PT 3000, Kinematica AG, Lucerne, Switzerland) along with a homogenizer generator of PT-DA 3030/4T, at a shear rate of 20,000 rpm (output energy 320 watt), at temperatures of 50, 60, 70, and 80°C for 1–6 h. The colors and the differences of chitosan solution were evaluated with the Hunter *L*, *a*, and *b* system using a colorimeter (TC-1800MK-II, Tokyo Denshoku, Tokyo, Japan); every sample measurement was repeated three times. The Hunter *L*, *a*, and *b* values were recorded. Hunter *L* represents the lightness on a scale of 0 (dark) to 100 (white); $+a$ the redness, $-a$ the greenness; $+b$ the yellowness and $-b$ the blueness. Mean *L*, *a*, and *b* values were used to determine the total color difference (ΔE) between the shearing treated and untreated chitosan solutions, by the following equation:

$$\Delta E = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{0.5} \quad (1)$$

where ΔL, Δa and Δb are the differences between *L*, *a*, and *b* values of the shearing treated chitosan solutions and the untreated chitosan solution.

Mechanical shearing without concurrent removal of small degraded fragments

Chitosan solution was prepared by dissolving 0.2%, 0.8%, 1.4%, and 2.0% (w/v) of chitosan in acetic acid buffer (0.2*M* acetic acid/0.1*M* sodium acetate). The solution was passed through the filter (Toyo Roshi Kaisha, 55 mm, Tokyo, Japan) to remove the insoluble materials. An aliquot of 700 mL filtrate in a glass vessel was placed in a water bath (Firstek, B403, Taipei, Taiwan) at a pre-set temperature. Mechanical shearing was operated with a homogenizer (Polytrom PT 3000, Kinematica AG, Lucerne, Switzerland) along with a homogenizer generator of PT-DA 3030/4T at a shear rate of 20,000 rpm (output energy 320 watt), 0 ± 1, 30 ± 1, and 50 ± 1°C for 1, 2, 3, 4, and 5 h.

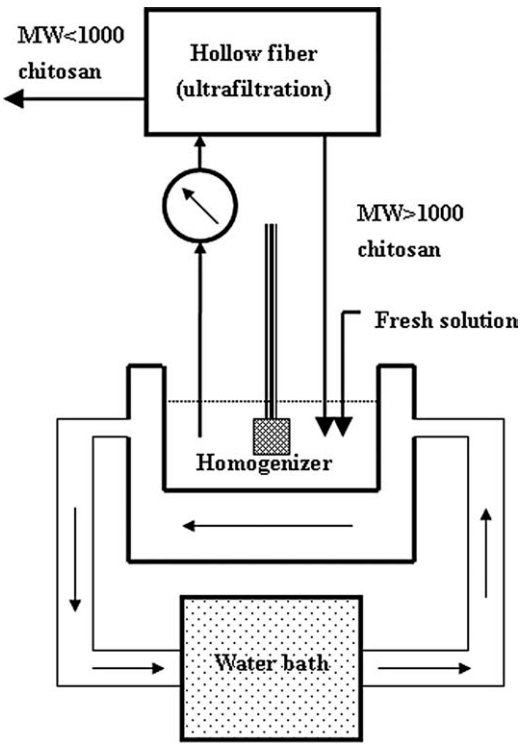

Figure 1 The configuration of homogenizer-ultrafiltration reactors.

Mechanical shearing with concurrent removal of small degraded fragments

During the mechanical shearing, the solution was circulated through an ultrafiltration spiral-wound cartridge with a cut-off size of 1,000 Da (Amicon CH2PRS system, Beverly, Mass.) to remove the degraded molecules (Fig. 1). The retentates were returned to the reactor for continuous treatment. Fresh solution equal to the volume of the elute was added at a pre-determined time to make up the reaction solution at constant volume.

Rate constant calculation

Degradation reaction by mechanical shearing is a first order reaction; its rate constant (k) can be obtained from eq. (2):[6,18,33,36]

$$1/M_t = 1/M_0 + kt/m = 1/M_0 + k't \quad (2)$$

where k is the rate constant (s^{-1}) of molecular weight degradation during mechanical shearing, k' is the pseudo-rate constant in mol g^{-1} s^{-1}, t is the

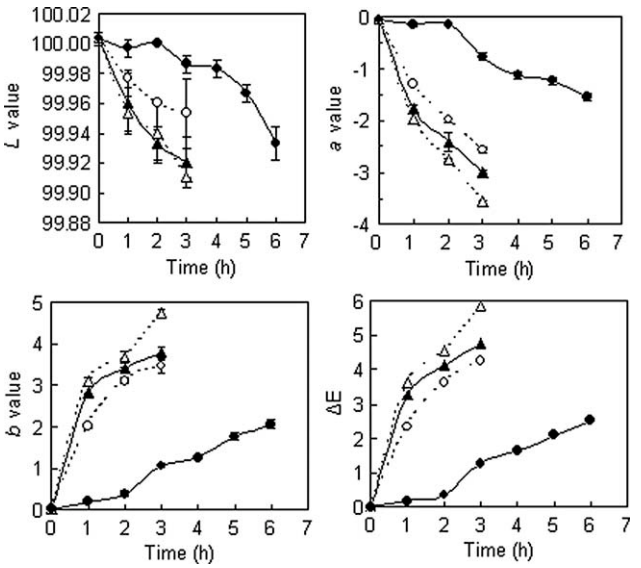

Figure 2 Effect of different treatment time on Hunter *L*, *a*, *b*, and ΔE value of chitosan solutions sheared at 50 (●), 60 (○), 70 (▲), and 80°C (△).

mechanical shearing time, M_0, and M_t are the weight average molecular weight of the chitosans before shearing and after shearing for t h, respectively, and m is the molecular weight of the chitosan monomer, $m = 167.7$ g mol^{-1}.

Statistical data analysis

Analysis of variance was used to determine any significant difference ($P < 0.05$). Duncan's new multiple range test was used to further test their difference by SAS/PC Program Version (SAS Institute, Cary, Ca., 1988)

RESULTS AND DISCUSSION

Effect of mechanical sheared temperature and time on color change of chitosan solution

Figure 2 shows the Hunter color parameters (*L*, *a*, *b*, and ΔE value) of chitosan solutions during mechanical shearing at 50, 60, 70, and 80°C for 1–6 h. The *L* values decreased over time for all treatment temperatures. The decreasing *a* values, with increasing treatment time, were more obvious for those treated at 60, 70, and 80°C than that at 50°C. In other words, chitosan solutions increased the greenness of these solutions treated in higher temperatures. However, the *b* values increased more obviously over time for these treated at 60, 70, and 80°C than that of 50°C, i.e., became more yellow in higher temperature solutions. The ΔE values also increased with increasing treatment time. The ΔE values of these treated at 60, 70, and 80°C had more noticeably increased than that of 50°C. The color darkening of the treated chitosan, as mentioned above, may be caused by the Maillard reaction.[29,30] The rate of browning was faster at higher temperature.[31] The Maillard reaction will consume the $-NH_2$ group; therefore, the functional group of chitosan chain will decrease. The color changes of sheared chitosan solutions were temperature and time-dependent. In conclusion, it is suggested that the degradation of chitosan solution by mechanical shearing should not exceed 50°C.

Effect of removing small degraded fragments by UF

Data in Figure 3 show that the molecular weight of the resultant products after mechanical shearing were smaller for those using UF to remove smaller degraded molecules concurrently during treatment than for that without UF treatment. The results indicated that the degradation were faster for those using UF treatment to remove smaller degraded molecules concurrently than those without UF treatment.

Figure 4 is the plot of the reciprocal of molecular weight and shearing time of 0.2% chitosan sheared at 50°C, with concurrent removal of small degraded fragments by UF treatment. Line 1 is the regression line of treatment from time 0 to 5 h. Equation (2) shows that the slope of the regression line is the pseudo-rate constants (k'); the rate constant (k) can be calculated from k'. The results of other different reaction temperatures, different concentration

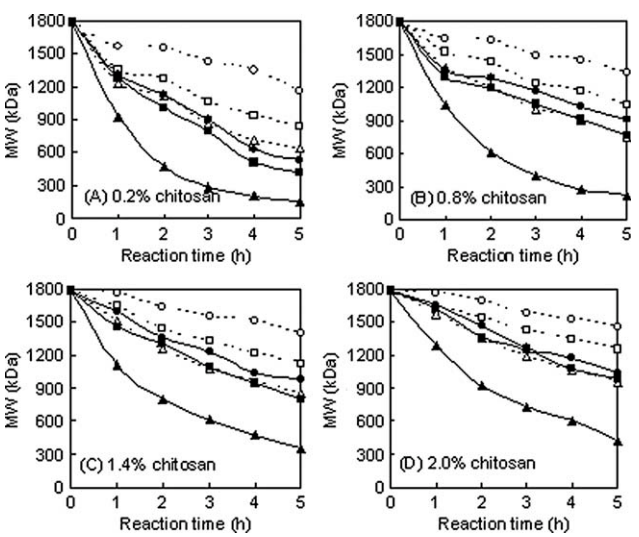

Figure 3 Changes of molecular weight (MW) of 0.2%, 0.8%, 1.4%, and 2.0% chitosan subjected to different times of shearing at 0 (●), 30 (■), and 50°C (▲). (The filled symbols are those for with concurrent UF treatment while the blank symbols are those for without concurrent UF treatment).

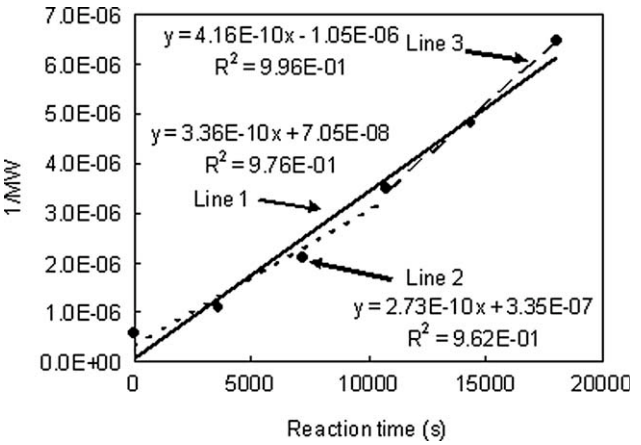

Figure 4 Plot of reciprocal of molecular weight (MW) of chitosan versus reaction time of shearing treatment of 0.2% chitosan solution at 50°C, and concurrent removing small degraded fragment by ultrafiltration treatment. Line 1, 2, and 3 are the regression line of treatment from time 0 to 5, 0–3, and 3–5 h, respectively.

solutions, or without concurrent UF treatment showed similar patterns. The rate constants calculated from Line 1 are listed in Table I.

Data in Table I show that the degradation rate constants were 1.8–6.0 times higher for those using UF to remove smaller degraded molecules concurrently during treatment than for that without UF treatment. It indicated that UF treatment facilitated the degradation reaction of mechanical shearing. It may be due to the efficiency of shearing degradation of higher molecular weight species increasing by the removal of smaller degraded fragments. With the mechanism of shearing degradation proposed, during the high rate of shearing, the polymer was sheared along the direction of the flow.[22] Besides the polymer being sheared at the high shear rate, Casale and Porter[23] reported the entangled molecules facilitated the degradation reaction during shearing treatment. Therefore, as mentioned above, the length of the polymer has to be long enough to be entangled and stretched apart from each other during shearing.[5] The chain length of smaller degraded fragment is not long enough to be entangled and stretched with other molecules to generate sufficient shear strength to tear the molecules apart. Those smaller degraded fragments collided with other molecules of either long or short chain length but could not generate enough strength to tear the molecules apart. The smaller fragments in the solution will only dissipate the shearing energy but generate no effective degradation reactions. For those concurrent UF treatments, the remaining molecules' chain length is long enough to be entangled and stretched apart from each other to generate the effective shearing to tear apart the molecules; therefore, the degradation rate constant increased by concurrent removal of small degraded fragments with UF treatment.

The rate constants were 1.0–2.0 and 1.3–1.6 times higher for that using UF treatment than for that without UF treatment using ultrasonic radiation and microfluidization to degrade the different concentrations (0.2–2.0%) 84% DD chitosan solutions at 0, 30, and 50°C.[18,26] The increased efficiency of UF treatment reported in this study (1.8–6.0 times) is higher than when using ultrasonic radiation and microfluidization. This may be due to the fact that the degradation mechanism of mechanical shearing differs from ultrasonic radiation and microfluidization. The mechanism of ultrasonic radiation and microfluidization are major results of cavitation and the free radical effect. However, the major results of the mechanism of mechanical shearing are the entanglement and tearing mentioned above. Therefore, mechanical shearing with the concurrent removal of small fragments by UF treatment can greatly improve the degradation efficiency.

TABLE I
Rate Constants (s^{-1}) of Different Concentrations Chitosan Solution that Were Sheared at 0, 30, and 50°C with or Without UF Treatment and Their Ratio

Temperature	0.2%	0.8%	1.4%	2.0%
0°C	2.50 E-09	1.68 E-09	1.46 E-09	1.24 E-09
0°C-UF[a]	1.25 E-08	4.66 E-09	4.53 E-09	3.82 E-09
(*k*-UF)/*k*[b]	5.0	2.8	3.1	3.1
30°C	5.80 E-09	3.69 E-09	3.15 E-09	2.15 E-09
30°C-UF	1.73 E-08	6.51 E-09	6.17 E-09	4.41 E-09
(*k*-UF)/*k*	3.0	1.8	2.0	2.1
50°C	9.41 E-09	6.81 E-09	5.80 E-09	4.53 E-09
50°C-UF	5.64 E-08	3.82 E-08	2.06 E-08	1.60 E-08
(*k*-UF)/*k*	6.0	5.6	3.6	3.5

[a] 0°C -UF represents chitosan was sheared at 0°C and concurrent UF treatment to remove small degraded fragments.
[b] (*k*-UF)/*k* represents the *k* of with UF treatment to divide the *k* of without UF treatment at same temperature.

TABLE II
Rate Constants (s^{-1}) of Different Concentration Chitosan Solutions that Were Sheared at 0, 30, and 50°C with or Without UF Treatment

	0°C	30°C	50°C	0°C-UF	30°C-UF	50°C-UF
0.2% chitosan						
k_a[a]	2.05 E-09	5.60 E-09	8.86 E-09	8.39 E-09	1.09 E-08	3.30 E-08
k_b[a]	2.08 E-09	5.92 E-09	9.19 E-09	1.81 E-08	2.62 E-08	8.87 E-08
k_b/k_a	1.0	1.1	1.0	2.2	2.4	2.7
0.8% chitosan						
k_a	1.67 E-09	3.67 E-09	6.74 E-09	4.43 E-09	5.80 E-09	3.05 E-08
k_b	1.78 E-09	3.82 E-09	7.36 E-09	5.52 E-09	8.50 E-09	4.53 E-08
k_b/k_a	1.1	1.0	1.1	1.3	1.5	1.8
1.4% chitosan						
k_a	1.40 E-09	3.09 E-09	5.75 E-09	4.08 E-09	5.40 E-09	1.64 E-08
k_b	1.61 E-09	3.29 E-09	8.84 E-09	4.83 E-09	7.43 E-09	2.83 E-08
k_b/k_a	1.2	1.1	1.0	1.2	1.4	1.7
2.0% chitosan						
k_a	1.11 E-09	2.15 E-09	4.39 E-09	3.56 E-09	4.01 E-09	1.27 E-08
k_b	1.30 E-09	2.20 E-09	4.61 E-09	4.06 E-09	5.03 E-09	2.33 E-08
k_b/k_a	1.2	1.0	1.1	1.1	1.3	1.8

[a] k_a is the rate constant of treatment from time 0 to 3 h; k_b is the rate constant of treatment from 3 to 5 h.

Effect of reaction time

The data in Figure 3 show that molecular weight of 0.2, 0.8, 1.4, and 2.0% chitosan decreased over time during the mechanical shearing for those either with or without concurrent UF treatment to remove the degraded small fragments at 0, 30, and 50°C. Similar degradation patterns have been reported in the literature regarding chitosan,[13,16,18] pullulan,[37] agarose, κ-carrageenan, and ι-carrageenan.[36]

In Figure 4, Lines 2 and 3 are the regression lines of treatment from time 0 to 3 h, and 3 to 5 h, respectively. These rate constants, k_a and k_b, calculated from Lines 2 and 3, respectively, are listed in Table II. Table II shows that k_a were slight smaller than k_b for those treated without concurrent removal of small degraded fragments by UF treatment, and k_a were remarkably smaller than k_b for those concurrently removing small degraded fragments by UF treatment. The results again showed the enhancing effect of increased degradation rate constant by concurrent removal of small degraded fragments by UF treatment.

Table II shows that concurrent UF treatment during shearing degradation 0.2–2.0% chitosan solutions at 50°C, k_b/k_a were between 1.7 and 2.7, larger than 1.3–2.4 at 30°C, in turn larger than 1.1–2.2 at 0°C. The results indicated that the rate constant increased with increasing solution temperature and the degradation rate constants did not decline with increased reaction time; this may be due to the majority of chitosan molecules remaining inside the reactor being high molecular weight species with concurrent UF treatment, in addition to the results of significant acid hydrolysis reaction taking place at higher solution temperature of 50°C;[38] the degradation rate did not slow down over time during mechanical shearing.

Decreases in degradation rate and rate constant along with degradation time have been reported in many polysaccharides, such as chitosan,[12,16] pullulan,[37] agarose, κ-carrageenan and ι-carrageenan.[36] However, the trend in Figure 4 is different, perhaps due to the concurrent removal of degraded small fragments by UF treatment during mechanism shearing degradation. Concurrent removal of degraded small fragments will increase the concentration of high molecular weight species remaining in the retention. The high molecular weight species increases the effective entanglement and tearing action during shearing.

Effect of chitosan concentration

Data in Figure 3 show that the molecular weight of the resultant product after mechanical shearing was the smallest for 0.2% chitosan solutions, and highest for 2% chitosan solutions, with or without the concurrent UF treatment. Data in Table I show that the solution concentration affected the degradation rate constant during mechanical shearing; the higher the solution concentration, the lower the reaction rate constant, with or without concurrent UF treatment.

Both results indicate that high concentration solution slows down the degradation reaction by shearing. Similar results have been reported on chitosan[9,12,18] and other polysaccharides.[36,39] Perhaps at the same energy level used to degrade the solution, the energy received by each molecule decreased as the solution concentration was increased or the chance to be degraded decreased, therefore slowing down the degradation reaction.

However, in practical mass production the solution needs the highest possible concentration to save

TABLE III
Effect of Chitosan Concentration on Degraded Efficiency of Shearing Combined Ultrafiltration Treated at 50°C

Chitosan concentration (%)	Ratio of concentration[a]	Ratio of MW[b]	Efficiency[c]
0.2	1.0	1.00	1.00
0.8	4.0	0.69	2.76
1.4	7.0	0.44	3.08
2.0	10	0.36	3.60

[a] Ratio of concentration: $C_x/C_{0.2}$, x are concentration of chitosan.
[b] Ratio of MW: $MW_{0.2}/MW_x$, x are concentration of chitosan.
[c] Efficiency = (ratio of concentration) × (ratio of MW).

energy and labor cost. In consideration of the unit mass production, the operation cost of the 2.0% solution is about 3.6 times cheaper than the 0.2% solution (Table III).

Effect of solution temperature

The molecular weight decreased faster (Fig. 3); the degradation rate constant increased with increasing solution temperature for four different concentrations solution, with or without concurrent UF treatment to remove small degraded fragments during mechanical shearing (Table I). This indicated that the chitosan molecules are degraded faster in solutions of higher temperature. The MWDR (molecular weight decrease ratio) of degraded chitosan by mechanical shearing was increased by the increasing reaction temperature.[9] The acid hydrolysis rate constant of chitosan was increased by the increasing solution temperature in 0.1*M* acetic acid and malic acid solution.[38] Chen et al.[13] reported that chitosan was degraded faster in solution of 40°C than that of 4°C and that the polydispersity was narrower in higher temperature solution. Lai et al.[40] reported that the hydrolysis rate constant of agarose and κ-carrageenan increased with increasing solution temperature. This may be due to acid hydrolysis reaction occurring concurrently during mechanical shearing. Another reason may be due to high solution temperature decreasing the solution viscosity. Lower solution viscosity will enhance the inter-molecular entanglement, elevating the tearing efficiency, thus increasing the degradation rate by mechanic shearing.

Rationale for proposing a practical mass production of chitosan

A combined method of mechanical shearing/UF treatment at 50°C and ultrasonic radiation or microfluidization/UF treatment, with both at 30°C, is proposed here for large industrial scale, in order to manipulate the molecular weight of chitosan to save on input energy and improve the efficiency.

The reasons for using mechanical shearing/UF treatment at 50°C at the first step are that high solution temperature of 50°C will decrease the solution viscosity and also limit the undesirable color change. There are two benefits to using mechanical shear/UF treatment at 50°C. The first one is decreasing solution viscosity with increasing temperature. The second is that high solution temperature should increase the acid hydrolysis reactions, thus improving the degradation rate constant because lower solution viscosity will enhance the intermolecular entanglements. This will elevate the tearing efficiency and increase the degradation rate resulting from mechanical shearing. Furthermore, the detrimental effects of high viscous solution (due to high concentration and high molecular weight of solute) on the cavitation effects during sonolysis or microfluidization can be circumvented. The reasons for proposing the use of ultrasonic radiation or microfluidization/UF treatment at 30°C for the second step are that the molecular weight of chitosan inside the reactor is not large enough to generate effective shearing to tear apart the molecules. The detrimental effect of high viscous solution for cavitation effects during sonolysis or microfluidization reactions will no longer exist because the molecular weight of chitosan has decreased and the solution temperature changed to 30°C to obtain high efficiency ultrasonic or microfluidization reaction environments.[18,26]

CONCLUSIONS

The degradation rate constants were 1.8–6.0 times higher for those concurrently using UF to remove smaller degraded molecules during treatment than that without UF treatment. The degradation rate constant increased with increasing solution temperature; however, the solution temperature should not exceed than 50°C to prevent the undesired color changes of the resulting product. A combined processing of mechanical shearing/UF treatment at 50°C and ultrasonic radiation or microfluidization/UF treatment at 30°C is proposed here for large industrial scale to manipulate the molecular weight of chitosan, thereby saving on input energy and improving the efficiency.

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