

# A study on Properties of aged chitosan solution

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## 1. INTRODUCTION

Chitosan is one of a few natural cationic polysaccharides that can be obtained by alkaline deacetylation of chitin which is the second most abundant polymeric material in the earth. Chitosan composed mainly of  $\beta$ -(1,4)-2-deoxy-2-amino-D-glucopyranose by (1  $\rightarrow$ 4)-linkages<sup>1</sup>].

Recently, chitin and chitosan have aroused attention for their biodegradability in vivo and biocompatibility<sup>2</sup>]. Also chitosan shows mild antimicrobial activity arising from its cationic residue<sup>3</sup>], which is an important property in view of the use of chitosan as a biomedical material<sup>4-8</sup>].

A large number of studies have been carried out to characterize chitosan in the state of solutions.

Jonathan Z. et al. summarized the relations between deacetylation values of chitosan and constant ( $K, \alpha$ ) for various solvent systems<sup>9</sup>]. M. Rinaudo, G. Pavlov and J. Desbrieres studied the influence of acid concentration on the solubilization of chitosan. The solubility of chitosan was observed in 16.5M acetic acid at  $\alpha \geq 0.5$  and a stoichiometric ratio [Acetic acid] / [Chitosan-NH<sub>2</sub>] = 0.6 and no salting out was observed on the addition of concentrated acetic acid<sup>10</sup>].

Carlos P., Carlos E. and Julio S. R. prepared interpolymer complexes of chitosan and polymethacrylic derivatives of salicylic acid and characterized<sup>5</sup>]. Xin C., Wenjun L. and Tongyin Y. blended chitosan with silk fibroin and found strong hydrogen bond between chitosan and silk fibroin by the study of infrared spectrum and X-ray diffractometry<sup>11</sup>].

Futhermore a number of studies indicate the high efficient forms of chitosan on the production of various sustained release drug carrier systems and wound healing processes such as solutions, gels, tablets, microparticles, foams and so on.

## 2. EXPERIMENTAL

### 2.1 Material

All materials used in this study were purchased as follows; acetic acid(99.7% Aldrich, U.S.A.), lactic acid(85% Aldrich, U.S.A.), urea(98% Aldrich, U.S.A.) and sodium hydroxide(98% Aldrich, U.S.A.).

Crab shell chitosan(Minimum 92% deacetylated) sample was purchased from Tae Hoon Bio Co. Ltd., KOREA and purified by the reprecipitation method.

Chitosan was dissolved in 1wt% acetic acid and filtered with glass filter paper. The solution

was neutralized with 1wt% sodium hydroxide solution. And solid state purified chitosan fragments were washed and dried in a vacuum at 60°C for 48 hours. Their viscosity at 0.5% solution in 0.5% acetic acid at 20°C was 105cps (MW ca.  $11.26 \times 10^4$ ), respectively. The molecular weights, shown in this report, were estimated on the basis of the data on a viscosity-molecular weight relations reported by Hiroi et al. and Tokura.

## 2.2 Preparation of Chitosan Solution

Chitosan powder dispersed in water at different feed ratio(0.5g/dl, 1g/dl). Then the chitosan powder was dissolved by adding lactic acid. Chitosan in acid media becomes a polyelectrolyte because of the protonation of the  $-NH_2$  groups.

Rinaudo M., Pavlov G. and Desbrieres j. reported the relation between acid concentration and the solubilization of chitosan[10].

Also, they reported that the complete solubilization of chitosan is obtained when the degree of protonation is around 0.5. It could be calculated the stoichiometry  $[Lactic\ acid] / [Chitosan-NH_2] = 0.7$ . So, to dissolve the amounts of 0.5g and 1g chitosan in 1dl water, 0.559g and 1.118g lactic acid required respectively.

In this study, 2wt% of lactic acid solution was used in preparing chitosan solutions.

## 2.3 Aging of Chitosan Solution

L. A. Nud'ga et al. investigated the time variation of the chitosan molecular characteristics by viscometry, sedimentation, rheology and polarized Light scattering in aqueous acetic acid solutions. And they suggested the existences of two competitive processes, namely, of the destruction and association of chitosan molecules[12].

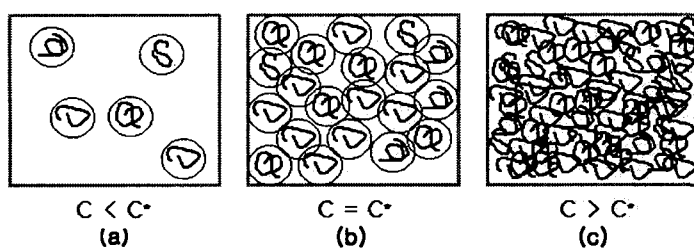


Fig. 1 Schematic of chain conformations in the (a) dilute, (b) transition, and (c) semi-dilute concentration regions[13]

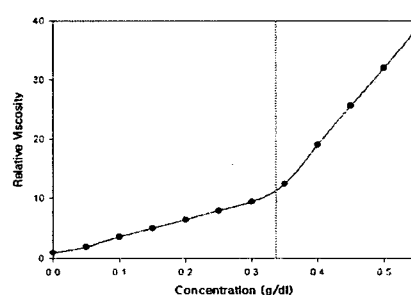


Fig. 2 Identification of transition concentration

Also such transition could be found in other polymer solutions in literature. For example, Loic H. and Dimitris V. investigated dynamics of hairy-rod polymer solution and found anisotropic ordering result from the interplay of particle interactions as a function of time in semi-dilute concentration regions[14]. The schematic of chain conformations shown in Fig. 1.

The transition concentration of chitosan was determined by viscometry method. The transition

concentration of chitosan, used in this study, is in the range of 0.30g/dl~0.35g/dl(shown in Fig. 2). So, each prepared chitosan solutions are in semi-dilute concentration region which is proper concentration to achieve molecular aggregation in solution state.

Each chitosan solution were aged at room temperature during 48 hour. A series of aged chitosan solutions were collected at every 2 hours and characterized by viscometry and DSC.

## 2.4 Characterization of Chitosan Solution

### 2.4.1 Viscometry

The viscosity of each aged chitosan solution was measured at  $30 \pm 0.03^\circ\text{C}$  using a Ubbelohde type capillary viscometer. The measured concentration of aqueous chitosan solution was 0.5g/dl.

### 2.4.2 Differential Scanning Calorimetry(DSC)

Various aged chitosan solutions were prepared for DSC experiments by accurately weighting 10mg of each sample and sealing this into liquid type aluminum pans. The pans were placed in a Perkins Elmer thermal analysis system and heated from  $-30^\circ\text{C}$  to  $150^\circ\text{C}$  at rate of  $5^\circ\text{C}/\text{min}$ . under a nitrogen atmosphere. From this thermal analysis, the melting points of each aged chitosan solutions were determined as a function of the aging time considered.

## 3. RESULT and DISCUSSION

### 3.1 Viscometry

The relative viscosity of each aged chitosan solution (Fig. 3) was measured at  $30 \pm 0.03^\circ\text{C}$  using a Ubbelohde type capillary viscometer. The measured concentration of aqueous chitosan solution was 0.5g/dl.

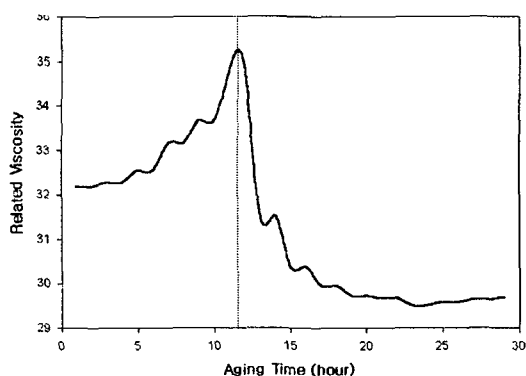


Fig. 3 Time variation of the relative viscosities of chitosan solution.

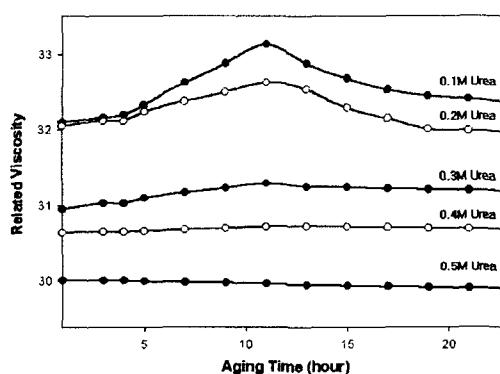


Fig. 4 The effect of urea content on the time dependant viscosity transition of chitosan solution.

The viscosity elevates with increasing the ageing time until 12 hours. But the viscosity of over 12 hours aged chitosan solution decreases with increasing the aging time. The effect of aging time on viscosity is very similar to the effect of aging time on thermal behavior of the solution. Both of these results, may reflect the kinetics of the molecular conformational stabilization process, is similar to L. A. Nud'ga et al. and Fangming G., Haishan B. and Ze Z. previous works[2,14].

It is possible that the first dissolved chitosan molecules in entangled random coil state form strongly swelled coil state. After that, the molecules separated from each other then disentangled chitosan molecules make more stable molecular conformations with water molecules and regularly arrange in a sheet-like structure[15]. The schematics of Possible molecular conformations which may accompany the harmonious transition of solution viscosities and melting points in solution state is shown in Fig. 5.

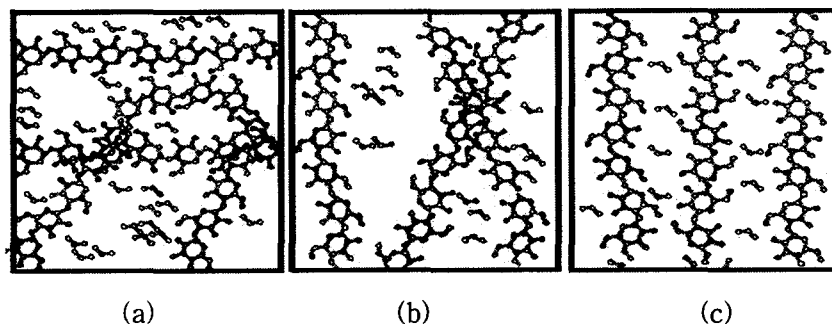


Fig. 5 Schematics of possible molecular conformations; (a) First dissolved chitosan molecules in random coil state form strongly swelled coil state, (b) Molecules separated from each other, (c) Molecules make more stable molecular conformations in a sheet-like structure.

To verify the driving force of this time affected transition in chitosan solution, It was investigated that the effect of adding urea, which is known to break hydrogen bonds[16], on the time affected viscosity transition. Fig. 4 shows the effect of urea content on the time dependant viscosity transition of chitosan solution. By increasing the content (from 0.1M to 0.5M) of urea in aqueous chitosan solution, the influence of aging time on solution viscosity decreases proportionally. Furthermore, the viscosity of more than 0.4M urea concentrated chitosan solution is not affected by aging time. From these results, it is possible that the driving force of such a time dependent transition is mainly the force of hydrogen bonding.

### 3.2 Differential Scanning Calorimetry(DSC)

Time variation of the molecular thermal characteristics was studied by DSC. DSC traces of the aged chitosan solutions are shown in Fig. 6

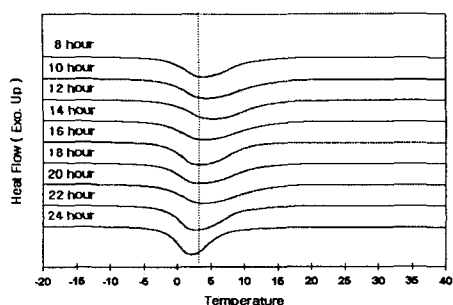


Fig. 6 DSC traces of aged chitosan solution

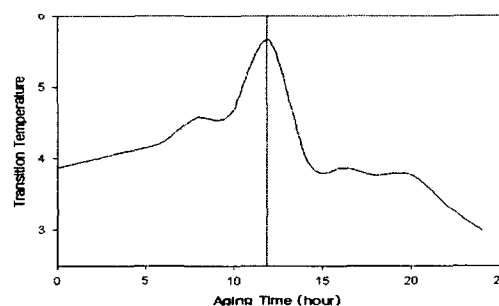


Fig. 7 The effect of aging time on the transition temperature of chitosan solution

And Fig. 7 shows the effect of aging time on the transition temperature of the aged mixtures. The transition point increases by the increasing aging time and the melting point of 12 hours aged chitosan solution is highest (5.66°C).

Then, the transition point of chitosan solutions, aged over 12 hours, decreases by the increasing the aging time.

It could be assumed from this result that the first dissolved chitosan molecules in entangled random coil state swells strongly. After that, the molecules separated from each other and make more stable molecular conformations just like the work of L. A. Nud'ga et al.[12].

#### 4. CONCLUSION

1. The melting point of 12 hours aged chitosan solution is highest (5.66°C). Also, viscosity of over 12 hours aged chitosan solution decreases by increasing the aging time.
2. From aging time over 12 hours, chitosan molecules made more stable conformations in a sheet-like structure by separating each other than before.(show in Fig. 5)
3. By increasing the content (from 0.1M to 0.5M) of urea in aqueous chitosan solution, the influence of aging time on solution viscosity decreases proportionally. Furthermore, the viscosity of more than 0.4M urea concentrated chitosan solution is not affected by aging time. From these results, it is possible that the driving force of such a time dependent transition is mainly the force of hydrogen bond.

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