VISCOELASTIC PROPERTIES
OF CHITOSAN

by

DOLORES MERCEDES RODRIGUEZ-SANCHEZ KIENZLE

B.S. Chemical Engineering
Universidad Metropolitana, Caracas, Venezuela (1976)

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Signature of Author

Department of Nutrition and Food Science
May, 1983.

Certified by

Dr. ChoKyun Rha
Thesis Supervisor

Accepted by

Dr. Steve R. Tannembaum
Chairman, Department Committee

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Submitted to the Department of Nutrition and Food Science on May 13, 1983, in partial fulfillment of the requirements for the Degree of Master of Science in Food Science.

ABSTRACT

The linear viscoelastic properties (G', G", η, H(τ)) of concentrated cationic polyelectrolyte solutions as affected by polymer concentration, pH and ionic strength were evaluated. Chitosan (2-amino,2-deoxy,β-(1-4) D glucan) was selected for this study because of its cationic nature and industrial potential. The modulus of the complex viscosity ranges from 8 poises to 500 poises at low frequency when chitosan concentration varies from 1.5 g/dl to 3.0 g/dl. The variability on the modulus of the complex viscosity values is attributed to the chitosan molecule extensibility in solution. Concentrated chitosan solutions show "pseudoplastic behavior" in the range of polymer concentration of 1.5 g/dl to 3.0 g/dl, pH between 3.0 and 5.0, and ionic strength of 0.2 M to 0.3 M. At chitosan concentrations above 2.5 g/dl a "gel-like" structure appears as indicated by the crossover of η" over η'. This phenomenon is related to an increase in the entanglement coupling as represented by the modulus of entanglement (Gₑₑ) with values between 1.3×10³ dyne/cm² and 1.8×10³ dyne/cm² for 3.0 g/dl chitosan solution and about 1.5×10² dyne/cm² for 1.5 g/dl chitosan concentration. It is also shown that the entanglement coupling is independent of the ionic strength of the media, however, it increases as pH is increased for high chitosan concentration, and remains unaltered by pH at low polymer concentration.

The logarithmic relationship between the relaxation spectrum function H(τ) and the time of relaxation is of -0.5 for short time of relaxation and -1.0 for longer times of relaxation. These two relationships, which are more likely to be present as chitosan concentration is decreased, indicated that during the short time frame, the relaxation mechanism of chitosan molecules under stress is primarily due to single strand motions. However, for longer periods the relaxation mechanism observed has been attributed to cooperative motion of entire portions of the "network".
The results of this study highlight the importance of the solution conditions as well as polymer concentration in the viscoelastic response of concentrated chitosan solutions.

Thesis Supervisor: Prof. ChoKyun Rha.
Title: Associated Professor of Biomaterials Science and Engineering.
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I am grateful to CONICIT for their financial support during my graduate studies.

Very special thanks to my husband Carlos, who always thought that I would succeed and gave me his unconditional love, friendship and support.

Finally, thanks to my parents, Juan and Dolores who always encouraged me to do my best.
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</tbody>
</table>
I. INTRODUCTION

Chitosan (2-amino, 2-deoxy, β-(1-4)D glucan) is a deacetylated derivative of chitin. The removal of some or all of the 2-acetyl groups from chitin molecules, by basic treatment, will impart the polycationic nature of chitosan. The polycationic nature of chitosan, as well as the wide spread renewable resources of chitinaceous materials, make the chitosan a biopolymer with great potential for industrial application.

Recently considerable efforts have been made to evaluate and establish the possible industrial application of chitosan. Thus, chitosan films have been studied for application in photography (Scott, 1977) and in selective permeation of ions and complexes (Blair and Ho, 1981; Masri et al., 1974). Also, the properties of chitosan molecules in solution have been tested in pulp and paper industry (Baranova et al., 1980; Johnson and Carlson, 1978).

The rheological behavior of chitosan, in both films and dilute solutions, has been evaluated. The relationship between mechanical properties-structure-mechanism of film formation has been established (Kienzle-Sterzer et al., 1980, 1982(a), 1982(b)). Also, the polyelectrolyte nature of chitosan in dilute solutions (Kienzle-Sterzer et al., 1982 (c)), as well as the influence of ionic strength on the
viscometric behavior of chitosan has been evaluated (Rodriguez-Sanchez et al., 1982).

The objective of this study is to determine the effect of polymer concentration, pH and ionic strength of the media on the linear viscoelastic response of chitosan in solution, at the concentrated region. Specifically this study is aimed at examining the linear viscoelastic parameters of concentrated chitosan solutions, (storage modulus (G'), loss modulus (G''), complex viscosity (η*) and the relaxation spectrum function H(τ) ) and to establish the role of inter- and intra-molecular interactions on the mechanism of response of chitosan molecules under shear, as affected by solution conditions (polymer concentration, pH and counter-ion concentration).
II. LITERATURE REVIEW

II.1 Chitosan

II.1.1 Sources and preparation.

Chitosan (2-amino, 2-deoxy, β(1-4) D glucan), Figure 1, was obtained for the first time by Hoppe-Seyler in 1894 when chitin was reacted with potassium hydroxide at 180 °C.

Chitin, the raw material from which chitosan is derived, is widely distributed in nature. Chitin is the most important structural polysaccharide for most invertebrates, as in the shell of insects, crabs, shrimps and others. Chitin has been also found associated to other polysaccharides in the fungal cell walls (Peberdy and Moore, 1975; Glaser and Brown, 1957), and with proteins in other animals (Hackman, 1960; Hackman, 1955).

Number of methods have been developed to obtain chitin and chitosan, for examples:

a) Extraction with NaOH (Rigby, 1936)

Crustacean wastes are treated with 40% NaOH solution at 115 °C for 6 hours under nitrogen atmosphere. After cooling, the mixture is filtered and washed with water until neutralized.
b) Melting with Potassium Hydroxide (Horowitz et al., 1957)

Chitin is melted with a mixture of solid potassium hydroxide and nickel under nitrogen enviroment at 180 °C. After half hour the melt is precipitated in ethanol and washed with water. This method renders almost 95% deacetylation of chitosan with a very low molecular weight.

c) Deacetylation with mixed solvents (Broussignac, 1968)

Chitin is deacetylated by a mixture of potassium hydroxide (50%), plus 96° ethanol (25%) and monoethyleneglycol (25%) at boiling temperature (120 °C). After 16 hours, the mixture is filtered and washed with water. Chitosan with approximately 83% of deacetylation is obtained.

However, it must be pointed out that the methods described above are not completely suitable for commercial production of chitosan. A general flow sheet of an industrial process used by Food, Chemicals & Research Laboratories, Ltd. is shown in Figure 2 (Muzzarelli, 1973).

II.1.2 Physical characteristics.

II.1.2.1 Solubility.

Chitosan is a hydrophilic polysaccharide, soluble in
FIGURE 2. INDUSTRIAL PROCESS OF CHITOSAN. (Muzzarelli, 1973).
dilute aqueous organic acid solutions, and insoluble in pure
water (Filar and Wirck, 1978; Muzzarelli, 1973). In the
process of solubilization the 2-amino group is protonated,
thus providing the polycationic nature of chitosan molecules
in solution.

Chitosan is also soluble in mixtures of water-ethanol,
water-acetone, and other solvent mixtures (Filar and Wirck,
1978). However, it is not soluble in sulfuric acid solu-
tions due to the formation of chitosan sulfate which is a
white crystalline precipitate.

II.1.2.2. Molecular weight,

The molecular weight of chitosan depends strongly on
the treatment of the raw material in the extraction of chi-
tin, as well as the deacetylation procedure used to obtain
chitosan.

Data on the polydispersivity of chitosan have been
determined in dilute acid (Strelina et al., 1979; Van Duin
and Hermans, 1959). According to these data, the poly-
dispersivity of chitosan, prepared at laboratory scale, is
between 1.24 and 2.0. However, data of polydispersivity of
chitosan manufactured commercially differs substantially as
shown in Table 1. This apparent discrepancy shows clearly
the importance of the method of preparation in the molecular
weight distribution of the final material.
TABLE 1
Molecular Weight Values for Chitosan Samples
Manufactured Commercially and Prepared in
0.33M Acetic Acid with 0.2M Sodium Acetate.*

<table>
<thead>
<tr>
<th>Commercial name</th>
<th>Mw x10^-3</th>
<th>Mn x10^-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kytex H</td>
<td>1302</td>
<td>198</td>
</tr>
<tr>
<td>Kytex L</td>
<td>110</td>
<td>51</td>
</tr>
<tr>
<td>J-I</td>
<td>1520</td>
<td>223</td>
</tr>
<tr>
<td>J-II-1</td>
<td>1685</td>
<td>203</td>
</tr>
<tr>
<td>J-II-2</td>
<td>1449</td>
<td>149</td>
</tr>
<tr>
<td>J-III</td>
<td>1750</td>
<td>289</td>
</tr>
<tr>
<td>RST-Co</td>
<td>315</td>
<td>80</td>
</tr>
<tr>
<td>MCI-17</td>
<td>3999</td>
<td>839</td>
</tr>
<tr>
<td>MCI-18</td>
<td>489</td>
<td>151</td>
</tr>
<tr>
<td>MCI-32</td>
<td>1871</td>
<td>414</td>
</tr>
<tr>
<td>Flonac-N</td>
<td>3686</td>
<td>101</td>
</tr>
<tr>
<td>FCRL 16-73</td>
<td>807</td>
<td>171</td>
</tr>
<tr>
<td>FCRL 4-74</td>
<td>233</td>
<td>67</td>
</tr>
<tr>
<td>FCRL 5-76</td>
<td>710</td>
<td>111</td>
</tr>
</tbody>
</table>

* A.C.M. Wu and W.A. Bough; 1978.
II.1.2.3. Viscosity.

a) Diluted chitosan solutions.

Viscosity of dilute chitosan solutions at low ionic strength has been studied (Kienzle-Sterzer et al., 1982(c)). This study indicates that the reduced viscosity of dilute chitosan solutions increases with dilution, as shown on Figure 3, where the polyelectrolytic nature of chitosan is demonstrated. However it was also shown (Rodriguez-Sanchez et al., 1982) that this behavior is suppressed as ionic strength of the media increases. The intrinsic viscosity of chitosan in solution has been evaluated as a function of several experimental conditions such as the degree of ionization and type of counter-ion (Kienzle-Sterzer et al., 1983(a); Rodriguez-Sanchez et al., 1982). Throughout these studies, it is indicated that chitosan is an extended molecule with flexibility which resembles that of sodium carboxymethyl cellulose.

The relationship between intrinsic viscosity and molecular weight of chitosan has been reported (Berkovich et al., 1980; Muzzarelli, 1977). Eventhough, the data from the literature appears to be contradictory, as by the constants of the Mark-Kuhn-Houwink equation $K_n = 8.93 \times 10^{-4}$, $a = 0.71$ (Muzzarelli, 1977) or $K_n = 72.8 \times 10^{-2}$, $a = 0.186$ (Berkovich et al., 1980), these values mainly indicate the importance of the intramolecular interactions, controlled by the solu-
Figure 3. Reduced viscosity (dl/gr) versus chitosan concentration (gr/dl) at different acetic acid concentration: • 1.7 x $10^{-3}$ M; ▲ 0.3 x $10^{-3}$ M; ◇ 1.7 x $10^{-2}$ M; ● 0.3 x $10^{-2}$ M; ▼ 1.7 x $10^{-1}$ M.
tion conditions, which in turn dictate the molecular conformation.

b) Concentrated chitosan solutions.

Rheological properties of concentrated chitosan solutions as affected by chitosan concentration have been reported (Kienzle-Sterzer, 1982(d); Sklyar et al., 1981). The results clearly indicated that the viscosity of chitosan solutions increase as concentration is increased and that increasing the shear rate leads to a decay in the viscosity. Also it has been reported that the changes of viscosity in chitosan solution with time are not due to acid degradation but to molecular rearrangements, which can be stabilized by increasing the ionic strength of the media.

II.1.2.4. Film properties.

The mechanical properties of chitosan films have been related to film preparation procedure and to film structure properties. The mechanical response of swollen chitosan films shows that chitosan films do not behave as ideal rubber-like materials. The non-ideality of chitosan films was represented by a negative slope on the plots of reduced stress versus the reciprocal of elongation. This negative deviation suggests that inter-molecular interactions increased with increasing strain (Kienzle-Sterzer et al., 1982(b); Kienzle-Sterzer, 1980). The orientation of chito-
san molecules in the film was studied with X-ray diffraction (Samuels, 1981).

The results of the stress relaxation and dynamic mechanical tests performed on films indicate the ionic nature of the bond responsible for the network formation (Kienzle-Sterzer et al., 1982(a) and 1982(b); Ogura et al., 1980). Stress relaxation experiments of swollen chitosan films in aqueous medium of different ionic strength (0.0 to 2.0 M NaCl) show that the modulus of elasticity increases with increasing ionic strength as a result of the electrostatic interactions between the chloride ions and the free electrons on the 2-amino group on the chitosan monomeric unit. Also, it is indicated that the relaxation times of swollen chitosan films are in the order of $10^4$ to $10^5$ seconds (Kienzle-Sterzer et al., 1982 (a) and (b)).

Relaxation times of this order of magnitude reveal the electrostatic nature of the bonds responsible for the relaxation process of the network under stress. Similar values of relaxation times have been reported for agar-agar and agarose gels (Watase and Arakawa, 1968; Arakawa, 1961).

Generally in these studies, the polyelectrolytic nature and the significance of solution conditions on the molecular conformation and mechanical response of chitosan have been indicated.
II.2 Viscoelasticity of polymer solutions.

Two main differences can be observed between a polymeric and a newtonian fluid when they are subject to small amplitude oscillatory shear experiment (Lodge, 1964):

a) The shear stress of the polymer solution oscillates with the same frequency of the shear rate, but it is out of phase. Newtonian fluids oscillate with the same frequency but the shear stress is in phase with the shear rate.

b) The existence of normal stresses which oscillate at a frequency \(2\omega\), with a non zero mean value.

Therefore the measurements of the amplitude and phase shift are used in order to describe the real an imaginary components of the shear rate and shear stress as a function of the frequency (Bird et al., 1977). Thus, the shear rate \(\dot{\gamma}\) will be calculated by:

\[
\dot{\gamma} = R_e \{ \dot{\gamma}^* \exp(i\omega t) \}
\]

Similarly the shear stress \(\tau\)

\[
\tau = R_e \{ \tau^* \exp(i\omega t) \}
\]

where: \(R_e\{\}\) represents the real part of the complex functions \(\dot{\gamma}^*\exp(i\omega t)\) and \(\tau^*\exp(i\omega t)\), for the complex shear rate and shear stress respectively,

\(\dot{\gamma}^*\) is the maximum amplitude of the strain

\(\tau^*\) is the maximum amplitude of the stress
\[ \omega \text{ is the frequency in radians/sec} \]
\[ t \text{ is time} \]

Therefore, if \( \dot{\gamma}^* \) is assumed real and positive, then

\[ \tau = -\eta' \gamma^* \cos \omega t - \eta'' \gamma^* \sin \omega t \]

where \( \eta' \) and \( \eta'' \) are the real and imaginary part of the complex viscosity (\( \eta^* \)) defined by analogy with newtonian fluids by:

\[ \eta^* = -\frac{\tau^*}{\dot{\gamma}^*} \]

The study of the dynamic viscoelastic properties of polymer solutions provide important information intrinsic to the system, because \( \eta \) as well as both the storage and loss moduli, \( (G') \) and \( (G'') \), defined as \( G' = \omega \eta'' \) and \( G'' = \omega \eta' \), are highly sensitive to the geometry of the flowing unit, as well as to the relaxation mechanism of the macromolecular system under oscillatory shear. For all these reasons, it is that the viscoelastic properties of polymeric material both in solution and solid state have been used to study the phenomenological behavior as well as molecules configuration of polymers (Ferry, 1980).
In order to describe theoretically the viscoelastic behavior of linear polymers in solution, several idealized models have been proposed:

a) Elastic dumbell model:

This model idealized the macromolecular backbone as an elastic dumbell of series of "beads" joined together by flexible springs (Kuhn, 1934). The main assumptions contained in this model are:

1. The "n" dumbells are suspended in a Newtonian fluid of viscosity $\eta_S$.

2. The friction coefficient ($f_o$) of the dumbells is given by the Stockes' law $f_o = -6\pi\eta_Sa$; where "a" is the beads radius.

3. The dumbells experience "Brownian motion" forces associated with thermal motion.

4. The inertial forces are neglegible.

5. The velocity distribution of the beads may be described by a Maxwellian distribution.

6. The solvent can be considered as a continuous.

Mainly two theories have been introduced to explain the linear viscoelastic behavior of dilute polymer solutions using the elastic dumbell model:

1) Theory of Rouse (Rouse, 1953)

This theoretical approach describes the polymer mole-
molecule as a series of beads-spring units where hydrodynamic interactions between the different submolecular junctions are neglected. Thus, from the Rouse's theory, the theoretical calculations of $G'$, $G''$ and the relaxation time of the polymer molecule are represented by the expressions:

$$G'(\omega) = n K T \sum_{p=1}^{n} \omega^2 \frac{\tau_p}{(1 + \omega^2 \tau_p^2)}$$

$$G''(\omega) = \omega \eta_s + n K T \sum_{p=1}^{n} \omega \frac{\tau_p}{(1 + \omega^2 \tau_p^2)}$$

$$\tau_p = \sigma^2 f_o / 24 K T \sin^2 \left[ \frac{p \pi}{2(N+1)} \right]$$

where: $n$ = the number of polymer molecules per unit volume.
$N$ = the number of submolecules in a molecule.
$\omega$ = frequency.
$\tau_p$ = relaxation time.
$K$ = Boltzmann constant.
$T$ = temperature.
$f_o$ = friction coefficient.

From these equations, for dilute polymer solutions that can be described by the Rouse's theory, the following direct relationships would be maintained:

At low values of frequency,

$$\log G'(\omega) \sim \log \omega^2$$
and

\[ \log G''(\omega) \sim \log \omega^1 \]

At high values of frequency,

\[ \log G'(\omega) = \log G''(\omega) \sim \log \omega^{0.5} \]


This theoretical model describes the polymer molecule as in the Rouse's model but it does consider the role of the hydrodynamic interactions between the beads. From this more realistic theoretical approach, the equations to calculate the theoretical values of \( G'(\omega) \) and \( G''(\omega) \) are comparable to those described on the Rouse's model. However, the expression for the relaxation time is modified according to Zimm's model as follow:

\[ \tau_k = 0.806 \eta_s a^3 P^{3/2} / \lambda_k K T \]

where:
- \( \eta_s \) = solvent viscosity
- \( \lambda_k \) = numerical coefficient (Zimm et al., 1956)
- \( P \) is calculated from

\[ \eta - \eta_s = 0.47 n \eta_s a^3 P^{3/2} \]

Therefore, the viscoelastic junctions of polymer molecules that can be described by Zimm's model must follow:

At low values of frequency,

\[ \log G'(\omega) \sim \log \omega^2 \]
and

\[
\log G''(\omega) \sim \log \omega^1
\]

At high value of frequency,

\[
\log G'(\omega) = \log G''(\omega) \sim \log \omega^{0.66}
\]

As it is here indicated the relationship of \(G'(\omega)\) and \(G''(\omega)\) and frequency at low frequencies is maintained if compared to the Rouse's model, however, at high frequency values the proportionality constant is altered. Several examples on the application of these theoretical approaches, for both charge and non-charge polymers, have been reported in the literature (Frangou et al., 1982; Okamoto et al., 1974; Amari and Nakamuro, 1973; Osaki and Schrag, 1971; Ferry, 1980)

b) Rigid dumbell model:

This model describe the macromolecular backbone in dilute solution as a dumbbell consists of spherical "beads" joined by a rigid rod. The other assumptions in this model are the same as those described for the elastic dumbell model.

The most used theory based on the rigid dumbell model is the Kirkwood-Auer theory (Kirkwood and Auer, 1951).

This theory represents the polymer molecule as a serie
of elements at equal intervals (b) on axis of length (L).
The Kirkwood-Auer theory predicts the following relationships between \(G'(\omega)\) and \(G''(\omega)\) with frequency (\(\omega\)):

\[
G'(\omega) = \left[ \frac{3 c R T}{5 M} \right] \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2}
\]

\[
G''(\omega) = \omega \eta_s + \left[ \frac{3 c R T}{5 M} \right] \omega \tau \left[ \frac{1}{1 + \omega^2 \tau^2 + 1/3} \right]
\]

where

\[
\tau = \pi \eta_s L^3 / 18 K T \ln(L/b)
\]

\(c = \text{polymer concentration}\)

\(\eta_s = \text{solvent viscosity}\)

\(R = \text{gas constant}\)

One of the advantages of the Kirkwood-Auer theory is that it predicts the linear viscoelastic response of stiff biopolymers such as helical polyaminoacids and proteins (Tanaka et al., 1967; Allis and Ferry, 1965) or shear-degraded DNA (Meyer et al., 1967).

Other theories that explain the linear viscoelastic response of dilute polymer solutions are the springy wormlike model (Harris and Hearst, 1966) and the damped torsional oscillator model (Tobolsky and Du Pre, 1969). These two theoretical approaches model the polymer chain in solu-
tion inbetween the flexible bead-spring model and the rigid rod model.

All the theories above outlined, deal directly with the linear viscoelastic response of dilute polymer solutions. Thus, intra-molecular and polymer-solvent interactions are responsible for the rheological behavior of the polymer chain. However, as polymer concentration is increased, inter-molecular interactions start to appear. Consequently, at highly concentrated solutions, intermolecular interactions are responsible for the viscoelastic behavior of the polymer molecule in solution. In this sense, it is expected that the molecular motion of polymer segments, under the influence of an external oscillatory stress, be rather complex. Thus, involving either inter-, intra-molecular interactions and polymer solvent interactions.

Some theoretical models are use to explain the linear viscoelastic response of concentrated polymer solutions:

1) The modified Rouse theory (Ferry et al., 1955)

This model uses the same assumptions of the Rouse's theory for dilute polymer solutions (Rouse, 1953). Here, the number of polymer molecules per unit volume is calculated from the density of the solution rather than from the polymer concentration. Therefore, the equations to calculate the storage and loss modulus are transformed to:
\[ G'(\omega) = \left[ \frac{\rho R T}{M} \right] \sum_{p=1}^{N} \omega^2 \tau_p^2 /(1 + \omega^2 \tau_p^2) \]

\[ G''(\omega) = \left[ \frac{\rho R T}{M} \right] \sum_{p=1}^{N} \omega \tau_p / (1 + \omega^2 \tau_p^2) \]

where \( \tau_p = 6 \eta M / \pi \rho R T \)

However, \( \tau_p \) is reduced to \( \tau_p = 6 \eta M / \pi \rho R T \) in the terminal zone of the frequency range where the solution properties are dictated by the terminal relaxation times.

2) Other theoretical approaches

Given the complexity of the concentrated polymer solutions other theoretical approaches have been proposed. These theories include other parameters, beside the theoretical considerations already stated in the above theory, such as the strength and characteristic of the junction responsible for the "network".

Generally, the network theories are based on the concept: motion of the junction. The following assumptions are considered in the "network" model:

a) The network is formed by strong local attractive forces.

b) The network can be considered as a macroscopic continuum.

c) The polymeric material is incompressible.
d) The junctions do not undergo thermal motions.

e) No terminal effects.

f) The end-to-end distance of any segment conforming the network follows a Gaussian distribution.

Based on these assumptions, several theories have been developed in order to evaluate the viscoelastic response of concentrated polymer solutions. Among those theories, the most commonly used are: Rubber-like elasticity theory (Staverman, 1962); Bueche theory (Bueche, 1954); Nakada theory (Nakada, 1955) and Chomppf-Duiser theory (Champff and Duiser, 1966).

The main common concept in all of these theories is the proportionality of one half between the logarithms of the relaxation function \( H(\tau) \) (calculated from \( G'(\omega) \) and \( G''(\omega) \)) and the time of relaxation. This theoretical proportionality has been found to apply to concentrated polymer solutions at short times of relaxation, generally related to motions of a single strand when affected by shear. Examples of some polymer solutions which follow this general relationship are reported in the literature (Ferry, 1980).

However, in some polymeric systems, as the time of relaxation is increased, deviations from this general relationship is observed. Chomppf Duiser theory (Chomppf and Duiser, 1966) obtained the following expressions to explain the relaxation spectrum function with the time of relaxa-
tion.

\[ H(\tau) = \left[ \frac{u R T}{2} \right] \left[ \frac{\tau_1}{\tau} \right]^{1/2} \]

for short times of relaxation, and

\[ H(\tau) = 1.56 \left[ \frac{u R T}{2} \right] \left[ \frac{\tau_1}{\tau} \right] \]

for \( \tau > 2.4 \tau_1 \) where

\[ \tau_1 = a^2 \left[ \frac{\rho}{u M_0} \right]^2 \frac{f_0}{6 \pi^2 K T} \]

- \( a \) = the size of the monomeric unit
- \( f_0 \) = frictional coefficient of the monomer
- \( u \) = polymer molar concentration per unit volume
- \( M_0 \) = monomeric molecular weight

This theoretical approach explains the relaxation mechanism of polymer molecules as a composite of:

- single strand motions at short relaxation time with \(-0.5\) relationship between the logarithms of the relaxation function and the time of relaxation, and cooperative motions extending over large portions of the network at long time of relaxation.

In general, the linear viscoelastic response of both dilute and concentrated polymer solutions provides the necessary information to evaluate the hydrodynamic behavior of polymer molecules under oscillatory stresses.
III. MATERIALS AND METHODS

III.1 MATERIALS

Chitosan, Madera Chitosan (Bio-Shell, Inc., Albany, Oregon) obtained from Tanner (snow) crab, Chionoecetes bairdi, with less than 1% of protein and ash, and with 80% deacetylation, was used in this study.

Analytical grade hydrochloric acid (Analytical reagent, Mallinckrodt. Inc. Kentucky) for chitosan solubilization, sodium hydroxide (Analytical reagent, Mallinckrodt. Inc. Kentucky) for pH adjustment, and sodium chloride (Fisher Scientific Company, New Jersey) to correct ionic strength, were used without further purification.

The molecular weight of chitosan was calculated from intrinsic viscosity of dilute chitosan solutions in 1% acetic acid, 2% LiCl at 25.0 ± 0.1 °C. The Mark-Kuhn-Houwink parameters used for the molecular weight determination were: (Berkovich et al., 1980)

\[ K_n = 72.8 \times 10^{-2} \]
\[ n = 0.186 \]

The estimated molecular weight for chitosan is 250,000 daltons.

III.2 EQUIPMENT
III.2.1. PH adjustment.

Measurements of pH were made using an Orion pH electrode model 91-02 connected to an Orion microprocessor pH/millivolt meter model 811 (Orion Research Inc., Cambridge, Ma.). The temperature of the system was 25.0 °C.

III.2.2. Rheological measurement.

The dynamic viscoelastic properties of concentrated chitosan solutions were determined by oscillatory shear experiments with the cone-plate arrangement of a Rheometric Mechanical Spectrometer (Rheometrics Inc. Union, N. J.).

The Rheometrics Mechanical Spectrometer (R.M.S.) is a rotational shear rheometer with interchangable test fixtures. It measures torque and normal forces over a wide range of both steady and dynamic shear. Table 2 shows the performance specification of the instrument.

III.3 METHODS


Chitosan solutions were prepared using hydrochloric acid (0.20 M) as solvent. To obtain a good dispersion, chitosan flakes were added slowly into the edge of the vortex of a strong stirred acid solution in order to minimize agglomeration. The addition of the chitosan flakes were completed before depletion of the vortex was accomplished.
Table 2

Performance Specification of Rheometrics Mechanical Spectrometer

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rotational Speed</td>
<td>$10^{-3} - 10^2$ rad/s</td>
</tr>
<tr>
<td>Speed Control</td>
<td>Analog</td>
</tr>
<tr>
<td>ERD Frequency</td>
<td>$10^{-3} - 200$ rad/s</td>
</tr>
<tr>
<td>Temperature Measurement</td>
<td>Thermocouple in contact with plate/cone</td>
</tr>
<tr>
<td>Oscillatory Shear Frequency</td>
<td>$10^{-2} - 500$ rad/s</td>
</tr>
<tr>
<td>Oscillatory Shear Strain</td>
<td>0.1 - 999%</td>
</tr>
<tr>
<td>Torque</td>
<td>10$^{-2}$ Nm full scale</td>
</tr>
<tr>
<td>Shear Stress</td>
<td>$10^{-3} - 10^3$ Pa</td>
</tr>
<tr>
<td>Normal Force</td>
<td>1N</td>
</tr>
<tr>
<td>Normal Stress</td>
<td>1 - $10^3$ Pa</td>
</tr>
</tbody>
</table>
After complete solubilization, the chitosan solutions were allowed to rest in a cool room at 2 °C for approximately 24 hours. Then NaCl was added to adjust the ionic strength to the desirable value (0.21 to 0.30 M). Immediately after, the solution was titrated in order to fix the pH between 3.0 to 5.0.

The general titration procedure was: 50 ml of stock chitosan solution was placed in a beaker where the electrode was immersed. The initial pH of the solution was recorded and a known volume of standard solutions of NaOH – NaCl was added under strong stirring. The new pH value was recorded once an equilibrium was reached. This procedure was repeated until the desirable pH value was obtained. Once titration was completed, the chitosan solution was kept at 2 °C for further testing.

III.3.2. Rheological measurements.

A sample of chitosan solution was placed in the gap between the cone and plate of the R.M.S.. The equipment fixtures selected in this study were:

Plate diameter= 50 mm

Cone angle= 0.019 radians

A 20% strain was fixed after checking the insensitivity of the complex viscosity/frequency with applied percentage of deformation.

Once the chitosan solution was placed in the gap of the
R.M.S. the values of the torque were recorded, as the cone performed the forced oscillations at increasing rate between 0.10 and 250 radians/sec. The resulting motion of the plate was automatically recorded by the instrument.

The storage ($G'$) and loss ($G''$) moduli were obtained from: (Walters, 1975)

\[
G' = \frac{-\omega S A \sin \phi}{A^2 - 2A \cos \phi + 1}
\]

\[
G'' = \frac{\omega S A (\cos \phi - A)}{A^2 - 2A \cos \phi + 1}
\]

where:
- $\omega$ = angular frequency of the oscillation.
- $A$ = amplitude obtained from the ratio between the angular amplitude of the plate and the angular amplitude of the cone.
- $\phi$ = phase lag of the plate behind the cone.

and $S$ is obtained by the expression:

\[
S = \frac{3 \beta (K - I \omega^2)}{2 \pi R^3 \omega}
\]

where:
- $\beta$ = cone-plate angle.
- $I$ = momentum of inertia of the plate.
- $K$ = restoring constant of the torsion wire.
- $R$ = radius of the plate.
The modulus of the complex viscosity ($|\eta^*|$) was calculated by the expression (Bird et al., 1977):

$$|\eta^*| = \left( (\eta')^2 + (\eta'')^2 \right)^{1/2}$$

where $\eta' = \text{the dynamic viscosity or viscous contribution, obtained by:}$

$$\eta' = G'' / \omega$$

and $\eta'' = \text{the elastic contribution, obtained by:}$

$$\eta'' = G' / \omega$$
IV. RESULTS

IV.1. Storage and loss moduli.

The storage modulus ($G'$), defined as the stress in phase with the strain divided by the strain (Ferry, 1980; Rivlin, 1956), is plotted against frequency in a logarithmic scale, for chitosan concentrations between 1.5 g/dl and 3.0 g/dl at pH from 3.0 to 5.0 and counter-ion concentration in the range of 0.2 to 0.3 M. The relationships of the logarithm of $G'$ in dyne/cm² and the logarithm of frequency ($\omega$) in sec⁻¹ are presented in Figures 4 to 19. These figures show that, for all experimental conditions, the storage modulus increases monotonically with increasing frequency. Also, it can be observed that the increase in $G'$ with increasing frequency is more steep for the lower chitosan concentrations. $G'$ increases from 8.0 dyne/cm² at a frequency of 100 sec⁻¹ to 50 dyne/cm² at 1000 sec⁻¹ for 1.5 g/dl chitosan concentration at pH 5.0 and 0.25 M ionic strength. On the other hand, $G'$ for 3.0 g/dl chitosan solution, under the same solution conditions, increases roughly from 200 dyne/cm² to 600 dyne/cm² for the same frequency range. On these figures, the dotted lines represent the theoretical relationship between $G'$ and $\omega$ according to the bead-spring model as predicted by the Rouse theory (Rouse, 1953).

Similarly, the loss modulus ($G''$), defined as the
Figure 4. Storage modulus for chitosan solutions as affected by frequency. Log \( G' \) versus log \( W \). PH 3.0, ionic strength 0.20 M. Chitosan concentration: \( \nabla = 1.5; \triangle = 2.0; \square = 2.5; \circ = 3.0 \) g/dl respectively.
Figure 5. Storage modulus for chitosan solutions as affected by frequency. Log $G'$ versus log $W$. PH 4.0, ionic strength 0.20 M. Chitosan concentration: ▼=1.5; △=2.0; □=2.5; ○=3.0 g/dl respectively.
Figure 6. Storage modulus for chitosan solutions as affected by frequency. Log $G'$ versus log $W$. PH 4.5, ionic strength 0.20 M. Chitosan concentration: $\nabla = 1.5; \Delta = 2.0; \square = 2.5; \bigcirc = 3.0$ g/dl respectively.
Figure 7. Storage modulus for chitosan solutions as affected by frequency. Log $G'$ versus log $W$. PH 5.0, ionic strength 0.20 M. Chitosan concentration: ▽=1.5; △=2.0; □=2.5; ○=3.0 g/dl respectively.
Figure 8. Storage modulus for chitosan solutions as affected by frequency. Log $G'$ versus log $W$. PH 3.0, ionic strength 0.21 M. Chitosan concentration: ▽ = 1.5; △ = 2.0; □ = 2.5; ○ = 3.0 g/dl respectively.
Figure 9. Storage modulus for chitosan solutions as affected by frequency. Log $G'$ versus log $W$. PH 4.0, ionic strength 0.21 M. Chitosan concentration: $\nabla = 1.5$; $\triangle = 2.0$; $\Box = 2.5$; $\bigcirc = 3.0$ g/dl respectively.
Figure 10. Storage modulus for chitosan solutions as affected by frequency. Log $G'$ versus log $W$. pH 4.5, ionic strength 0.21 M. Chitosan concentration: ▽=1.5; △=2.0; □=2.5; ○=3.0 g/dl respectively.
Figure 11. Storage modulus for chitosan solutions as affected by frequency. Log $G'$ versus log $W$. PH 5.0, ionic strength 0.21 M. Chitosan concentration: $\updownarrow = 1.5$; $\Delta = 2.0$; $\square = 2.5$; $\bigcirc = 3.0$ g/dl respectively.
Figure 12. Storage modulus for chitosan solutions as affected by frequency. Log G' versus log W. PH 3.0, ionic strength 0.25 M. Chitosan concentration: ▽ = 1.5; △ = 2.0; □ = 2.5; ○ = 3.0 g/dl respectively.
Figure 13. Storage modulus for chitosan solutions as affected by frequency. Log $G'$ versus log $W$. PH 4.0, ionic strength 0.25 M. Chitosan concentration: $\nabla$=1.5; $\Delta$=2.0; $\square$=2.5; $\bigcirc$=3.0 g/dl respectively.
Figure 14. Storage modulus for chitosan solutions as affected by frequency. Log $G'$ versus log $W$. PH 4.5, ionic strength 0.25 M. Chitosan concentration: $\nabla = 1.5$; $\Delta = 2.0$; $\Box = 2.5$; $\bigcirc = 3.0$ g/dl respectively.
Figure 15. Storage modulus for chitosan solutions as affected by frequency. Log G' versus log W. PH 5.0, ionic strength 0.25 M. Chitosan concentration: ▽=1.5; △=2.0; □=2.5; ○=3.0 g/dl respectively.
Figure 16. Storage modulus for chitosan solutions as affected by frequency. Log $G'$ versus log $W$. pH 3.0, ionic strength 0.30 M. Chitosan concentration: $\nabla = 1.5$; $\Delta = 2.0$; $\square = 2.5$; $\bigcirc = 3.0$ g/dl respectively.
Figure 17. Storage modulus for chitosan solutions as affected by frequency. Log $G'$ versus log $W$. PH 4.0, ionic strength 0.30 M. Chitosan concentration: ▽ = 1.5; △ = 2.0; □ = 2.5; ○ = 3.0 g/dl respectively.
Figure 18. Storage modulus for chitosan solutions as affected by frequency. Log $G'$ versus log $W$. PH 4.5, ionic strength 0.30 M. Chitosan concentration: $\nabla=1.5; \Delta=2.0; \Box=2.5; \bigcirc=3.0$ g/dl respectively.
Figure 19. Storage modulus for chitosan solutions as affected by frequency. Log $G'$ versus log $W$. PH 5.0, ionic strength 0.30 M. Chitosan concentration: ▽=1.5; △=2.0; □=2.5; ○=3.0 g/dl respectively.
stress 90° out of phase with the strain divided by the strain (Ferry, 1980; Rivlin, 1956), plotted logarithmically against the frequency is shown in Figures 20 to 35. Likewise to G', the loss modulus (G'') increases monotonically with increasing frequency and the increase is steepest for the lower polymer concentrations. On these figures, the dotted lines represent the theoretical relationship between G'' and ω according to the bead-spring model as predicted by the Rouse theory (Rouse, 1953).

IV.2. Complex viscosity

Complex viscosity (|η*|) is defined as the ratio of the stress in phase with the rate of strain divided by the rate of strain (Ferry, 1980). The complex viscosity usually is represented by a real component (η') and an imaginary component (η'') as:

\[ η^* = η' + iη'' \]

where

η': represents the viscous contribution to the system.

η'': represents the elastic contribution to the system.

Both η' and η'' can be calculated from the experimental values of the storage and loss moduli by the expressions:
Figure 20. Loss modulus for chitosan solutions as affected by frequency. Log $G''$ versus log $W$. PH 3.0 ionic strength 0.20 M. Chitosan concentration: ▽=1.5; ▲=2.0; ■=2.5; ◆=3.0 g/dl respectively.
Figure 21. Loss modulus for chitosan solutions as affected by frequency. Log $G''$ versus log $W$. PH 4.0 ionic strength 0.20 M. Chitosan concentration: ▽=1.5; △=2.0; ■=2.5; ◆=3.0 g/dl respectively.
Figure 22. Loss modulus for chitosan solutions as affected by frequency. Log $G''$ versus log $W$. PH 4.5 ionic strength 0.20 M. Chitosan concentration: ▼=1.5; ▲=2.0; ■=2.5; ○=3.0 g/dl respectively.
Figure 23. Loss modulus for chitosan solutions as affected by frequency. Log $G''$ versus log $W$. PH 5.0 ionic strength 0.20 M. Chitosan concentration: ▽=1.5; △=2.0; □=2.5; ◇=3.0 g/dl respectively.
Figure 24. Loss modulus for chitosan solutions as affected by frequency. Log $G''$ versus log $W$. PH 3.0 ionic strength 0.21 M. Chitosan concentration: $\nabla=1.5; \Delta=2.0; \square=2.5; \circ=3.0$ g/dl respectively.
Figure 25. Loss modulus for chitosan solutions as affected by frequency. Log $G''$ versus log $W$. PH 4.0 ionic strength 0.21 M. Chitosan concentration: ▽=1.5; ▲=2.0; ■=2.5; ◊=3.0 g/dl respectively.
Figure 26. Loss modulus for chitosan solutions as affected by frequency. Log $G''$ versus log $W$. PH 4.5 ionic strength 0.21 M. Chitosan concentration: ▼=1.5; ▲=2.0; ■=2.5; ○=3.0 g/dl respectively.
Figure 27. Loss modulus for chitosan solutions as affected by frequency. Log $G''$ versus log $W$. PH 5.0 ionic strength 0.21 M. Chitosan concentration: $\nabla$=1.5; $\Delta$=2.0; $\Box$=2.5; $\bullet$=3.0 g/dl respectively.
Figure 28. Loss modulus for chitosan solutions as affected by frequency. Log $G''$ versus log $W$. PH 3.0 ionic strength 0.25 M. Chitosan concentration: $\nabla=1.5$; $\Delta=2.0$; $\Box=2.5$; $\bigcirc=3.0$ g/dl respectively.
Figure 29. Loss modulus for chitosan solutions as affected by frequency. Log $G''$ versus log $W$. PH 4.0 ionic strength 0.25 M. Chitosan concentration: $\nabla=1.5$; $\Delta=2.0$; $\blacksquare=2.5$; $\bullet=3.0$ g/dl respectively.
Figure 30. Loss modulus for chitosan solutions as affected by frequency. Log $G''$ versus log $W$. PH 4.5 ionic strength 0.25 M. Chitosan concentration: $\nabla=1.5; \Delta=2.0; \square=2.5; \Theta=3.0$ g/dl respectively.
Figure 31. Loss modulus for chitosan solutions as affected by frequency. Log $G''$ versus log $W$. PH 5.0, ionic strength 0.25 M. Chitosan concentration: $\nabla=1.5$; $\Delta=2.0$; $\square=2.5$; $\bullet=3.0$ g/dl respectively.
Figure 32. Loss modulus for chitosan solutions as affected by frequency. Log $G''$ versus log $W$. PH 3.0 ionic strength 0.30 M. Chitosan concentration: $\nabla = 1.5$; $\triangle = 2.0$; $\blacksquare = 2.5$; $\circ = 3.0$ g/dl respectively.
Figure 33. Loss modulus for chitosan solutions as affected by frequency. Log $G''$ versus log $W$. PH 4.0 ionic strength 0.30 M. Chitosan concentration: $\nabla =1.5$; $\Delta =2.0$; $\square =2.5$; $\bullet =3.0$ g/dl respectively.
Figure 34. Loss modulus for chitosan solutions as affected by frequency. Log $G''$ versus log $W$. PH 4.5 ionic strength 0.30 M. Chitosan concentration: $\Delta = 1.5$; $\Delta = 2.0$; $\Delta = 2.5$; $\Delta = 3.0$ g/dl respectively.
Figure 35. Loss modulus for chitosan solutions as affected by frequency. Log $G''$ versus log $W$. PH 5.0 ionic strength 0.30 M. Chitosan concentration: $\nabla = 1.5; \Delta = 2.0; \Box = 2.5; \bigcirc = 3.0$ g/dl respectively.
(Bird et al., 1977)

\[ \eta' = \frac{G'}{\omega} \]

\[ \eta'' = \frac{G''}{\omega} \]

where "\( \omega \)" is the rate of shear in radians/sec.

The logarithm of the complex viscosity plotted against the logarithm of frequency in sec\(^{-1}\), is shown in Figures 36 to 51. These figures show that the complex viscosity of concentrated chitosan solutions decreases with increasing frequency. This "pseudoplastic" behavior of the solutions is more pronounced for high chitosan concentrations, and diminishes as chitosan concentration is decreased.

The wide range of the values of complex viscosity, varying from approximately 10 poises for 1.5 g/dl chitosan solution (pH = 3.0 and Cl\(^-\) = 0.25 M) to almost 400 poises for 3.0 g/dl chitosan solution (pH = 5.0 and Cl\(^-\) = 0.25 M) indicates the highly variable nature of the chitosan molecules in solution. The extensible nature of the molecule is evidenced when the complex viscosities are compared. The chitosan solution of concentration 3 g/dl at ionic strength of 0.2 M has a complex viscosity of 120 poises at pH 3.0 while at pH 5.0 the complex viscosity is 280 poises. This extensive molecular capacity has been observed previously in dilute chitosan solutions with the expansion factor \( \alpha_{\eta_e} \) obtained from intrinsic viscosity. The value of the expan-
Figure 36. Frequency dependence of the modulus of complex viscosity of chitosan solutions. Log $|\eta^*|$ versus log $W$. PH 3.0, ionic strength 0.20 M. Chitosan concentration: ▽ = 1.5; ▲ = 2.0; ▼ = 2.5; • = 3.0 g/dl respectively.
Figure 37. Frequency dependence of the modulus of complex viscosity of chitosan solutions. Log |\eta^*| versus log \(W\). PH 4.0, ionic strength 0.20 M. Chitosan concentration: \(\nabla=1.5\); \(\Delta=2.0\); \(\Box=2.5\); \(\bigcirc=3.0\) g/dl respectively.
Figure 38. Frequency dependence of the modulus of complex viscosity of chitosan solutions. Log $|\eta^*|$ versus log $W$. PH 4.5, ionic strength 0.20 M. Chitosan concentration: $\nabla = 1.5; \bigtriangleup = 2.0; \blacksquare = 2.5; \bullet = 3.0$ g/dl respectively.
Figure 39. Frequency dependence of the modulus of complex viscosity of chitosan solutions. Log $|\eta^*|$ versus log $W$. pH 5.0, ionic strength 0.20 M. Chitosan concentration: ▽=1.5; △=2.0; □=2.5; ○=3.0 g/dl respectively.
Figure 40. Frequency dependence of the modulus of complex viscosity of chitosan solutions. $\log |\eta^*|$ versus $\log W$. PH 3.0, ionic strength 0.21 M. Chitosan concentration: $\nabla$=1.5; $\Delta$=2.0; $\square$=2.5; $\bullet$=3.0 g/dl respectively.
Figure 41. Frequency dependence of the modulus of complex viscosity of chitosan solutions. Log |\(\eta^*\)| versus log W. pH 4.0, ionic strength 0.21 M. Chitosan concentration: ▽ = 1.5; ▲ = 2.0; ▼ = 2.5; ○ = 3.0 g/dl respectively.
Figure 42. Frequency dependence of the modulus of complex viscosity of chitosan solutions. Log|η*| versus log W. PH 4.5, ionic strength 0.21 M. Chitosan concentration: ▼=1.5; ▲=2.0; ▼=2.5; ◆=3.0 g/dl respectively.
Figure 43. Frequency dependence of the modulus of complex viscosity of chitosan solutions. Log |η*| versus log W. PH 5.0, ionic strength 0.21 M. Chitosan concentration: ▽=1.5; △=2.0; □=2.5; ★=3.0 g/dl respectively.
Figure 44. Frequency dependence of the modulus of complex viscosity of chitosan solutions. Log |\eta| versus log W. PH 3.0, ionic strength 0.25 M. Chitosan concentration: ▼=1.5; ▲=2.0; ▼=2.5; ●=3.0 g/dl respectively.
Figure 45. Frequency dependence of the modulus of complex viscosity of chitosan solutions. Log $|\eta^*|$ versus log $W$. PH 4.0, ionic strength 0.25 M. Chitosan concentration: $\nabla=1.5$; $\Delta=2.0$; $\blacksquare=2.5$; $\bigcirc=3.0$ g/dl respectively.
Figure 46. Frequency dependence of the modulus of complex viscosity of chitosan solutions. Log $|\eta^*|$ versus log $W$. pH 4.5, ionic strength 0.25 M. Chitosan concentration: $\nabla = 1.5$; $\Delta = 2.0$; $\Box = 2.5$; $\circ = 3.0$ g/dl respectively.
Figure 47. Frequency dependence of the modulus of complex viscosity of chitosan solutions. Log |\(\eta^*\)| versus log \(W\). PH 5.0, ionic strength 0.25 M. Chitosan concentration: \(\nabla=1.5\); \(\Delta=2.0\); \(\square=2.5\); \(\circ=3.0\) g/dl respectively.
Figure 48. Frequency dependence of the modulus of complex viscosity of chitosan solutions. Log $|\eta^*|$ versus log $W$. PH 3.0, ionic strength 0.30 M. Chitosan concentration: ▽=1.5; △=2.0; □=2.5; ○=3.0 g/dl respectively.
Figure 49. Frequency dependence of the modulus of complex viscosity of chitosan solutions. Log |\eta^*| versus log W. pH 4.0, ionic strength 0.30 M. Chitosan concentration: ▽ = 1.5; ▲ = 2.0; ■ = 2.5; ○ = 3.0 g/dl respectively.
Figure 50. Frequency dependence of the modulus of complex viscosity of chitosan solutions. Log |η*| versus log W. PH 4.5, ionic strength 0.30 M. Chitosan concentration: ▼=1.5; ▲=2.0; ■=2.5; ○=3.0 g/dl respectively.
Figure 51. Frequency dependence of the modulus of complex viscosity of chitosan solutions. Log |\( \eta^* \) | versus log W. pH 5.0, ionic strength 0.30 M. Chitosan concentration: \( \nabla =1.5; \bigtriangleup =2.0; \blacktriangle =2.5; \bigcirc =3.0 \) g/dl respectively.
sion factor for chitosan ranged from 1.85 at pH 5.0 and ionic strength of 0.50 M to 3.60 at pH 3.0 and ionic strength of 0.05 M (Kienzle-Sterzer et al., 1983(a)). Also, it has been reported in literature for other polysaccharides (carboxymethyl cellulose, methylcellulose and sodium alginate), at equivalent concentration in solution, viscosity values comparable to the values obtained for chitosan solutions (Kuroiwa et al., 1967; Amari and Nakamura, 1970 and 1971).

In order to evaluate the effect of pH on $\eta'$ and $\eta''$, the values for $\eta'$ and $\eta''$ are plotted versus pH for each of the selected ionic strength between 0.2 M and 0.3 M and presented in Figures 56 to 59 and Figures 60 to 63. These figures show that for the higher chitosan concentrations, both $\eta'$ and $\eta''$ increase with increasing pH at low frequency values, however, this tendency is diminished as the shear rate is increased (i.e. no pH effect is observed at 3300 sec$^{-1}$). Also, these figures indicate that the effect of pH on $\eta'$ and $\eta''$ is reduced as chitosan concentration is decreased. Such behavior is clearly demonstrated by $\eta'$ and $\eta''$ being nearly independent on pH for 1.5 g/dl chitosan solutions at frequencies between 83 and 3300 sec$^{-1}$.

IV.3. Relaxation spectrum

In order to study the relaxation behavior of chitosan as it is affected by the polymer concentration, pH and
Figure 56. Frequency dependance of real component ($\eta'$) of complex viscosity as affected by pH. Ionic strength 0.20 M. Chitosan concentration:

- $\bigcirc$: $\Delta$: $\square$: $\nabla$: $\eta'$ = 1.5;
- $\bullet$: $\Delta$: $\blacksquare$: $\nabla$: $\eta'$ = 2.0;
- $\blacklozenge$: $\Delta$: $\blacktriangle$: $\nabla$: $\eta'$ = 2.5;
- $\bigcirc$: $\Delta$: $\blacklozenge$: $\nabla$: $\eta'$ = 3.0 g/dl respectively.
Figure 57. Frequency dependence of real component ($\eta'$) of complex viscosity as affected by pH. Ionic strength 0.21 M. Chitosan concentration:
- $\circ$: $\triangle$: $\square$ : $\gamma$ = 1.5;
- $\bullet$: $\Delta$: $\square$: $\gamma$ = 2.0;
- $\bigcirc$: $\bigtriangleup$: $\square$: $\gamma$ = 2.5;
- $\bigstar$: $\triangle$: $\square$: $\gamma$ = 3.0 g/dl respectively.
Figure 58. Frequency dependence of real component ($\eta'$) of complex viscosity as affected by pH. Ionic strength 0.25 M. Chitosan concentration: ○: Δ: □: △: ▽ = 1.5; ○: Δ: □: △: ▽ = 2.0; ○: Δ: □: △: ▽ = 2.5; ○: Δ: □: △: ▽ = 3.0 g/dl respectively.
Figure 59. Frequency dependence of real component ($\eta'$) of complex viscosity as affected by pH. Ionic strength 0.30 M. Chitosan concentration:
- $\diamondsuit$: $\Delta$: $\nabla$: $\nabla$ = 1.5;
- $\odot$: $\Delta$: $\nabla$: $\nabla$ = 2.0;
- $\odot$: $\Delta$: $\nabla$: $\nabla$ = 2.5;
- $\odot$: $\Delta$: $\nabla$: $\nabla$ = 3.0 g/dl respectively.
Figure 60. Frequency dependance of imaginary part (η") of the complex viscosity as affected by pH. Ionic Strength 0.20 M. Chitosan concentration:
Ο:Δ:□:▽=1.5; Ω:Δ:□:▽=2.0; Ω:Δ:□:▽=2.5; Ω:Δ:□:▽=3.0 g/dl respectively.
Figure 61. Frequency dependance of imaginary part ($\eta^*$) of the complex viscosity as affected by pH. Ionic Strength 0.21 M. Chitosan concentration: ○:Δ: □: ▽ =1.5; ○:Δ: □: ▽ =2.0; ○:Δ: □: ▽ =2.5; ○:Δ: □: ▽ =3.0 g/dl respectively.
Figure 62. Frequency dependence of imaginary part ($\eta''$) of the complex viscosity as affected by pH. Ionic Strength 0.25 M. Chitosan concentration: $\bigcirc$ : $\Delta$ : $\square$ : $\nabla$ = 1.5; $\bigcirc$ : $\Delta$ : $\square$ : $\nabla$ = 2.0; $\bigcirc$ : $\Delta$ : $\square$ : $\nabla$ = 2.5; $\bigcirc$ : $\Delta$ : $\square$ : $\nabla$ = 3.0 g/dl respectively.
Figure 63. Frequency dependance of imaginary part ($\eta''$) of the complex viscosity as affected by pH. Ionic Strength 0.30 M. Chitosan concentration: O: A: □: ▲: V = 1.5; O: A: □: ▲: V = 2.0; O: A: □: ▲: V = 3.0 g/dl respectively.
ionic strength, the relaxation spectrum function, $H(\tau)$, was calculated (Ferry, 1980),

a) from the storage modulus ($G'$):

$$H(\tau) = \frac{dG'}{d\ln \omega} + \frac{1}{2} \frac{d^2G'}{d(\ln \omega)^2} \bigg| \frac{1}{\omega} = \sqrt{2\tau}$$

when the slope of $H(\tau)$ is positive

and

$$H(\tau) = \frac{dG'}{d\ln \omega} - \frac{1}{2} \frac{d^2G'}{d(\ln \omega)^2} \bigg| \frac{1}{\omega} = \tau / \sqrt{2\tau}$$

when the slope of $H(\tau)$ is negative.

b) from the loss modulus ($G''$):

$$H(\tau) = \frac{2}{\pi} \left[ G'' + \frac{dG''}{d\ln \omega} \right] \bigg| \frac{1}{\omega} = \sqrt{3\tau}$$

when the slope of $H(\tau)$ is positive

and

$$H(\tau) = \frac{2}{\pi} \left[ G'' - \frac{d^2G''}{d(\ln \omega)^2} \right] \bigg| \frac{1}{\omega} = \tau$$

when the slope of $H(\tau)$ is negative

Figures 73 to 88 show the logarithmic relationship of $H(\tau)$ in dyne/cm$^2$ and the time of relaxation $\tau$ in sec. From these figures, it can be observed that the values of the relaxation spectrum function calculated from $G'$ and from $G''$
falls on the same line, therefore no second approximation is needed in order to evaluate the relaxation spectrum (Graessly et al., 1977; Hlavacek and Kotrba, 1967; Roesler and Twyman, 1955). These figures, (Figure 73-88), show that for the higher chitosan concentration (3 g/dl) the logarithm of \( H(\tau) \) is proportional to the logarithm of the reciprocal of the square root of the time of relaxation. Such proportionality is maintained for almost all the frequency range independent of pH and ionic strength of the solution. However, as chitosan concentration is decreased, deviation from this relationship is observed. As the chitosan concentration is decreased, lower values of the logarithm of \( H(\tau) \) are obtained and deviation begins to appear at lower values of the time of relaxation.

Changes in the mechanism of relaxation have been related to deviations on the relationship of the logarithm of \( H(\tau) \) to the reciprocal square root of the logarithm of the time of relaxation (Chompff and Duijer, 1966; Duijer and Staverman, 1965), therefore, the Figures 73 to 88 strongly indicate the importance of the environmental conditions as well as chitosan concentration on the relaxation of the chitosan molecules under stress.
Figure 73. Relaxation spectrum function - time of relaxation relationship. Log $H(\tau)$ versus $\tau$. Ionic strength 0.20 M, pH 3.0. Chitosan concentration: $\blacktriangle$: $\triangledown = 1.5$ $\blacktriangledown$: $\triangle = 2.0$; $\blacktriangleleft$: $\square = 2.5$; $\bullet$: $\bigcirc = 3.0$ g/dl respectively. Dark symbol: from $G''(w)$, Empty symbol: from $G'(w)$.
Figure 74. Relaxation spectrum function – time of relaxation relationship. \( \log H(\tau) \) versus \( \tau \). Ionic strength 0.20 M, pH 4.0. Chitosan concentration: \( \nabla: \nabla = 1.5 \) \( \Delta: \Delta = 2.0 \); \( \square: \square = 2.5 \); \( \circ: \circ = 3.0 \) g/dl respectively. Dark symbol: from \( G''(\omega) \). Empty symbol: from \( G'(\omega) \).
Figure 75. Relaxation spectrum function - time of relaxation relationship. Log $H(\tau)$ versus $\tau$. Ionic strength 0.20 M, pH 4.5. Chitosan concentration: $\nabla$: $\nabla = 1.5$, $\Delta$: $\Delta = 2.0$; $\square$: $\square = 2.5$; $\bigcirc$: $\bigcirc = 3.0$ g/dl respectively. Dark symbol: from $G''(w)$. Empty symbol: from $G'(w)$. 
Figure 76. Relaxation spectrum function - time of relaxation relationship. Log $H(\tau)$ versus $\tau$. Ionic strength 0.20 M, pH 5.0. Chitosan concentration: $\triangledown$: $\triangleleft$=1.5 $\Delta$: $\triangle$=2.0; $\square$: $\Box$=2.5; $\bigcirc$: $\bigcirc$=3.0 g/dl respectively. Dark symbol: from $G''(w)$. Empty symbol: from $G'(w)$. 
Figure 77. Relaxation spectrum function - time of relaxation relationship. Log H(τ) versus τ. Ionic strength 0.21 M, pH 3.0. Chitosan concentration: ▽: ▽=1.5 △: △=2.0; □: □=2.5; ○: ○=3.0 g/dl respectively. Dark symbol: from G"(w). Empty symbol: from G'(w).
Figure 78. Relaxation spectrum function - time of relaxation relationship. Log H(τ) versus τ. Ionic strength 0.21 M, pH 4.0. Chitosan concentration: ▼: ▽ = 1.5 ▲: △ = 2.0; ■: □ = 2.5; ○: ◊ = 3.0 g/dl respectively. Dark symbol: from G''(w). Empty symbol: from G'(w).
Figure 79. Relaxation spectrum function - time of relaxation relationship. Log $H(\tau)$ versus $\tau$. Ionic strength 0.21 M, pH 4.5. Chitosan concentration: ▼: $\gamma = 1.5$ ▲: $\Delta = 2.0$; ■: □ = 2.5; ○: □ = 3.0 g/dl respectively. Dark symbol: from $G''(w)$. Empty symbol: from $G'(w)$.
Figure 80. Relaxation spectrum function – time of relaxation relationship. Log $H(\tau)$ versus $\tau$. Ionic strength 0.21 M, pH 5.0. Chitosan concentration: ▼: ▼ = 1.5 ▲: ▲ = 2.0; ■: ■ = 2.5; ○: ○ = 3.0 g/dl respectively. Dark symbol: from $G''(w)$. Empty symbol: from $G'(w)$. 
Figure 81. Relaxation spectrum function - time of relaxation relationship. Log H(τ) versus τ. Ionic strength 0.25 M, pH 3.0. Chitosan concentration: ▼: △ = 1.5
△: △ = 2.0; □: □ = 2.5; ○: ○ = 3.0 g/dl respectively. Dark symbol: from G''(w).
Empty symbol: from G'(w).
Figure 82. Relaxation spectrum function - time of relaxation relationship. Log $H(\tau)$ versus $\tau$. Ionic strength 0.25 M, pH 4.0. Chitosan concentration: ▼: $\Delta = 1.5$ ◼: $\Delta = 2.0$; ▲: $\square = 2.5$; ◌: $\odot = 3.0$ g/dl respectively. Dark symbol: from $G''(w)$. Empty symbol: from $G'(w)$. 
Figure 83. Relaxation spectrum function - time of relaxation relationship. Log H(τ) versus τ. Ionic strength 0.25 M, pH 4.5. Chitosan concentration: ▼: ▼ = 1.5 ▲: ▲ = 2.0; ■: ■ = 2.5; ○: ○ = 3.0 g/dl respectively. Dark symbol: from G''(w). Empty symbol: from G'(w).
Figure 84. Relaxation spectrum function - time of relaxation relationship. Log $H(\tau)$ versus $\tau$. Ionic strength 0.25 M, pH 5.0. Chitosan concentration: ▼:▼=1.5 △:△=2.0; ■:■=2.5; ○:○=3.0 g/dl respectively. Dark symbol: from $G''(w)$. Empty symbol: from $G'(w)$. 
Figure 85. Relaxation spectrum function - time of relaxation relationship. Log $H(\tau)$ versus $\tau$. Ionic strength $0.30\ M$, $pH\ 3.0$. Chitosan concentration: ▼: ▼=1.5
▲: ▲=2.0; □: □=2.5; ○: ○=3.0 $g/dl$ respectively. Dark symbol: from $G''(w)$.
Empty symbol: from $G'(w)$. 
Figure 86. Relaxation spectrum function – time of relaxation relationship. Log H(τ) versus τ. Ionic strength 0.30 M, pH 4.0. Chitosan concentration: ▼: ▼=1.5
▲: ▲=2.0; □: □=2.5; ○: ○=3.0 g/dl respectively. Dark symbol: from G'(w).
Empty symbol: from G''(w).
Figure 87. Relaxation spectrum function - time of relaxation relationship. Log $H(\tau)$ versus $\tau$. Ionic strength 0.30 M, pH 4.5. Chitosan concentration: ▼: $\nabla$=1.5 ▲: $\Delta$=2.0; ■: □=2.5; ○: O=3.0 g/dl respectively. Dark symbol: from $G''(w)$. Empty symbol: from $G'(w)$. 
Figure 88. Relaxation spectrum function - time of relaxation relationship. Log $H(t)$ versus $\tau$. Ionic strength 0.30 M, pH 5.0. Chitosan concentration: $\nabla$: $\nabla$=1.5, $\triangle$: $\triangle$=2.0; $\square$: $\square$=2.5; $\bigcirc$: $\bigcirc$=3.0 g/dl respectively. Dark symbol: from $G''(w)$. Empty symbol: from $G'(w)$. 
V. DISCUSSION

Linear viscoelastic material functions, \((G', G'' \text{ and } \eta^*)\), measured at small amplitude forced oscillation shear flow experiments, were used to study the rheological behavior of concentrated chitosan solutions, as affected by both polymer concentration and the solution conditions (pH and ionic strength).

The storage modulus \(G'(\omega)\), defined as the stress in phase with the strain divided by the strain, is a measure of the energy stored and recovered per cycle. Meanwhile, the loss modulus \(G''(\omega)\), defined as the stress 90° out of phase with the strain divided by the strain, is a measure of the energy dissipated or loss during the harmonic deformation (Ferry, 1980; Rivlin, 1956). The analysis of these two material functions, \((G'(\omega) \text{ and } G''(\omega))\), at the same frequency range, will provide important information on the characteristics of the system under evaluation.

The relationship between the logarithm of \(G'\) and \(G''\) with the logarithm of frequency is presented in Figures (4 to 19) and (20 to 35) respectively. These figures indicate that \(G'\) as well as \(G''\) increase with increasing frequency, for all the experimental conditions. The observed increase in \(G'\) and \(G''\) values is steeper at low chitosan concentration than for the higher concentrations. However, such tendency is diminished when frequency is increased, as shown by the
square root relationship between both G' and G" with respect to frequency (represented by the dotted lines on Figures 4 to 35) at the high shear rates. This phenomenon, which is observed independent of the solution condition, indicates that a change in the nature of cooperative motion of the chains occurs as frequency increases at the lower polymer concentration. However, as chitosan concentration is increased, this suggested change becomes gradually less evident. Similar behavior has been reported for other polymeric systems with mobile junctions (Chompff and Duiser, 1966; Duiser and Staverman, 1965; Bueche, 1955; Ferry et al., 1955). A detailed discussion on the differences in the relaxation process of chitosan molecules under shear will be discussed in relation to the relaxation spectrum.

In order to quantify the energy dissipative effects of alternating stress, it is useful to define the complex viscosity (η*) as the ratio of the stress in phase with rate of strain divided by the rate of strain (Ferry, 1980). Figures 36 to 51, the logarithm of the modulus of the complex viscosity plotted against the logarithm of frequency, showed the increase of the complex viscosity with increasing concentration. These figures also reveal the "pseudoplastic" nature of the chitosan solutions for all the conditions examined. In spite of the decrease of the modulus of the complex viscosity with increasing frequency, the decay seems to be more pronounced as the chitosan concen-
concentration is increased.

The "pseudoplastic" behavior of concentrated chitosan solutions has been related to the molecular reorientation under shear. This reorientation phenomena affects the inter- and intra-molecular interactions between neighboring segments. For a given ionic strength and pH, as chitosan concentration increases the reorientation under shear is increased, which is enhanced by a decrease on the ionization degree of the molecules due to an increasing polymer concentration in addition to the effect due to higher polymer concentration by itself (Figures 36 to 51). On the other hand, the repulsive electrostatic interactions on the chitosan backbone become progressively greater with dilution, preventing the reorientation process. The relationship between polymer concentration and the degree of ionization of chitosan molecules in solution has been studied by potentiometric titration experiments. (Kienzle-Sterzer et al., 1983(b)).

Figures 52 to 55 exhibit the relationship between the modulus of the complex viscosity with polymer concentration. These figures also show the effect of frequency and pH for a given counter-ion concentration. It is clearly indicated by these figures that the dependance of $|\eta^*|$ on chitosan concentration and pH is diminished as frequency is increased. Thus, the difference in the modulus of the complex viscosity at 3300 sec$^{-1}$, for a given chitosan con-
Figure 52. Polymer concentration dependance of the modulus of complex viscosity for chitosan solutions. $|\eta^*|$ versus chitosan concentration at 0.20 M ionic strength. $\circ=83$; $\square=530$; $\Delta=3300$ sec$^{-1}$ respectively. Open symbol: pH=3.0; dark symbol: pH=5.0.
Figure 53. Polymer concentration dependence of the modulus of complex viscosity for chitosan solutions. $|\eta^*|$ versus chitosan concentration at 0.21 M ionic strength. 

- $\bigcirc$ = 83; $\Box$ = 530; $\Delta$ = 3300 sec$^{-1}$ respectively. 
- Open symbol: pH=3.0; dark symbol: pH=5.0.
Figure 54. Polymer concentration dependence of the modulus of complex viscosity for chitosan solutions. $|\eta^*|$ versus chitosan concentration at 0.25 M ionic strength. ○=83; □=530; Δ=3300 sec$^{-1}$ respectively. Open symbol: pH=3.0; dark symbol: pH=5.0.
Figure 55. Polymer concentration dependence of the modulus of complex viscosity for chitosan solutions. $|\eta^*|$ versus chitosan concentration at 0.30 M ionic strength. $\bigcirc=83$; $\square=530$; $\bigtriangleup=3300\ \text{sec}^{-1}$ respectively. Open symbol: pH=3.0; dark symbol: pH=5.0.
centration, between pH 3.0 and 5.0 is almost neglectable compared with the difference in $|\eta^*|$ at 83 sec$^{-1}$, under the same conditions. This phenomena suggests that at high frequencies only segmental motions are involved, however, at low frequencies more involved are the overall motions which extend over larger portions of the molecule or system, which in turn are more likely to be affected by the solution conditions.

It is convenient to express the complex viscosity in function of its components as: (Bird et al., 1977)

$$\eta^* = \eta' + i\eta''$$

where the real part ($\eta'$) can be considered as the viscous contribution, and the imaginary part ($\eta''$) as the elastic component. Figures 56 to 59 and 60 to 63 show the influence of pH, for various polymer concentrations and ionic strength, at selected frequencies between 83 sec$^{-1}$ and 3300 sec$^{-1}$, on $\eta'$ and $\eta''$ respectively. As these figures indicate, both $\eta'$ and $\eta''$ increase as pH increases at low frequencies, nevertheless, an increase in frequency lessens such dependance. This behavior is made more evident as chitosan concentration is increased. Likewise, a decrease in the components of the complex viscosity with increasing shear rate is more pronounced for the higher polymer concentrations. Moreover, a combined plott of $\eta'$ and $\eta''$ as a
Figure 64. Frequency dependence of complex viscosity components (\(\eta'\) and \(\eta''\)) as affected by pH. Ionic strength 0.21 M. O = 83; Δ = 530; □ 1300; ▽ = 3300 reciprocal seconds respectively. Empty symbol: \(\eta'\); dark symbol: \(\eta''\).
Figure 65. Frequency dependence of complex viscosity components ($\eta'$ and $\eta''$) as affected by pH. Ionic strength 0.30 M. $\bigcirc$ = 83; $\Delta$ = 530; $\square$ 1300; $\nabla$ = 3300 reciprocal seconds respectively. Empty symbol: $\eta'$; dark symbol: $\eta''$. 
function of pH (Figures 64 and 65) shows that $\eta''$ crossover
$\eta'$ at high pH (~4.5) for chitosan concentrations above 2.5
g/dl. Such "crossover" indicates that increasing chitosan
concentration increases the entanglement coupling to the
point of a "gel-like" structure where $\eta''$ is larger than $\eta'$.

Similar phenomenon has been observed in some polysac-
carides such as Xantam Gum (Frangou et al., 1982), and
synthetic polymers as polyisobutylene and poly-n-octyl
methacrylate (Marvin and Oser, 1962; Chompff and Prins,
1968). However, as shear rate is increased, this gel-like
state induced by pH and chitosan concentration tends to
dissappear. Therefore, once more the predominant effect of
shear in the reorientation process (as indicated previously
when the effect of frequency on the complex viscosity was
discussed) is evidenced.

Two important parameters can be calculated from $G'$ and
$G''$; the storage compliance ($J'$) and the loss compliance
($J''$)' defined as (Ferry, 1980):

$$J'(\omega) = \frac{G'(\omega)}{\left[G'(\omega)\right]^2 + \left[G''(\omega)\right]^2}$$

$$J''(\omega) = \frac{G''(\omega)}{\left[G'(\omega)\right]^2 + \left[G''(\omega)\right]^2}$$

The relationships of $J'(\omega)$ with $G'(\omega)$ and $J''(\omega)$ with
$G''(\omega)$ are represented in Figures 66 and 67 respectively.
Figure 66. Storage compliance $J'(\omega)$ - Storage modulus $G'(\omega)$ relationship curve.
Figure 67. Loss compliance $J''(w)$ - Loss modulus $G''(w)$ relationship curve.
Because both storage and loss modulus are monotonic functions of frequency, which are easily normalized by polymer concentration when concentration-frequency superposition is obeyed (Kienzle-Sterzer et al., 1982(d)), the compliances were plotted against G' and G" rather than frequency. Therefore, the relationship between J'(ω) and G'(ω), as well as J"(ω) and G"(ω), will provide a master-like curve almost independent of chitosan concentration. As can be observed on Figures 66 and 67, all the experimental points follow the same pattern independently of chitosan concentration, pH and ionic strength. Such findings clearly demonstrate that, eventhough the solution conditions affect the viscoelastic properties of concentrated chitosan solutions, the relaxation mechanism is the same in all the conditions used in this study.

In order to quantify the entanglement on viscoelastic solutions the following parameter is defined (Sanders et al., 1968)

\[
G_{en} = \frac{2}{\pi} \int_{-\infty}^{+\infty} G''(\omega) \, d\ln\omega
\]

where \(G_{en}\) is the modulus of entanglement. Figures 68 to 71 show \(G_{en}\) as a function of pH and chitosan concentration for a given ionic strength. These figures show that \(G_{en}\) increases with increasing chitosan concentration and pH.
Figure 68. pH dependence of the modulus of entanglement $G_e$ for chitosan solutions. Ionic strength 0.20 M.
Figure 69. PH dependence of the modulus of entanglement $G_{en}$ for chitosan solutions. Ionic strength 0.21 M.
Figure 70. PH dependence of the modulus of entanglement $G_e$ for chitosan solutions. Ionic strength 0.25 M.
Figure 71. PH dependence of the modulus of entanglement $G_e$ for chitosan solutions. Ionic strength $0.30 \text{ M}$. 
Figure 72. Ionic strength dependance of the modulus of entanglement $G_\text{en}$ as affected by pH and chitosan concentration. PH: III: III: III: III = 3.0; \( \Delta: \Delta: \Delta: \Delta = 4.0; \) III: III: III: III = 5.0.
This behavior indicates that the entanglement coupling increases with decreasing degree of ionization (Kienzle-Sterzer et al., 1983(b)), thus, demonstrate a significant effect of the repulsive electrostatic forces between charged points on the chitosan backbone upon the entanglement network formation. Figure 72 shows the relationship between $G_{en}$ and ionic strength of the media. $G_{en}$ remains independent of the counter-ion concentration in the experimental range. This phenomenon may be explained by the decrease in the number of counter-ions bound per glucosamine residue with increasing chitosan concentration, as shown by the counter-ion activity coefficient in semiconcentrated solutions (Kienzle-Sterzer et al., 1983). Therefore, an increase in repulsive forces between the counterions clouds surrounding the chitosan backbone, caused by an increase in the overlapping by increasing polymer concentration, makes that the amount of counterions bound per monomer be controlled by chitosan concentration rather than the salinity of the solution. Consequently, finite changes in ionic strength should not alter the viscoelastic response of chitosan in concentrated solutions.

Finally, in order to study the relaxation mechanism in concentrated chitosan solutions, the relaxation spectrum obtained from both $G'(\omega)$ and $G''(\omega)$, is plotted logarithmically against the time of relaxation. Figures 89 to 92 show the relaxation spectrum obtained experimentally as well
Figure 89. Relaxation spectrum function – time of relaxation relationship according to the theoretical prediction of ChomP-H-Duiser theory. Ionic strength 0.21 M, pH 3.0. Chitosan concentration: ▼: ▼=1.5; ▲: △=2.0; ■: □=2.5; ○: ○=3.0 g/dl respectively. Dark symbol: from G"(w). Empty symbol: from G'(w). ----: slope = -0.5 ; -.--.-: slope = -1.
Figure 90. Relaxation spectrum function - time of relaxation relationship according to the theoretical prediction of Chompol-Duiser theory. Ionic strength 0.21 M, pH 5.0. Chitosan concentration: ▼: ▼=1.5; △: △=2.0; □: □=2.5; ○: ○=3.0 g/dl respectively. Dark symbol: from $G''(w)$. Empty symbol: from $G'(w)$. ----: slope = -0.5 ; --.--.--.: slope = -1
Figure 91. Relaxation spectrum function - time of relaxation relationship according to the theoretical prediction of ChompH-Duiser theory. Ionic strength 0.25 M, pH 3.0. Chitosan concentration: ▽: ▽=1.5; △: △=2.0; ■: ■=2.5; ○: ○=3.0 g/dl respectively. Dark symbol: from G"(w). Empty symbol: from G'(w). ----: slope = -0.5 ; --..--..: slope = -1
Figure 92. Relaxation spectrum function - time of relaxation relationship according to the theoretical prediction of ChompaH-Duizer theory. Ionic strength 0.30 M, pH 5.0. Chitosan concentration: ▼: ▼ = 1.5; ▲: ▲ = 2.0; ■: ■ = 2.5; ○: ○ = 3.0 g/dl respectively. Dark symbol: from G"(w). Empty symbol: from G'(w). -.-.: slope = -0.5 ; -.-.-.: slope = -1
as the theoretical relationship calculated according to Chompff - Duijer theory (Chompff and Duijer, 1966) where:

\[ H = f(\tau^{-1/2}) \quad \text{for } \tau < 2.4\tau_1 \]

and

\[ H = f(\tau^{-1}) \quad \text{for } \tau > 2.4\tau_1 \]

From the Figures 89 to 92, we can see that at high frequencies, which correspond to short times, \( H \) is proportional to \( \tau^{-1/2} \). Such relationship has been theoretically related with motions within a single strand with negligible hydrodynamic interactions in both dilute and concentrated polymer solutions (Chompff and Duijer, 1966; Harris and Hearst, 1966; Holders et al., 1956; Ferry et al., 1955; Rouse, 1953). On the other hand, the observed depndancy of \( H \) to \( \tau^{-1} \) has been related to cooperative motions of whole portions of the system (Chompff and Duijer, 1966).

These two different behaviors which occur in concentrated chitosan solutions are explained as follow: The molecular motions at low frequencies, for lower chitosan concentration, are strongly restricted by the electrostatic repulsion between charged points on the chitosan backbone. As the polymer concentration is increased, the degree of ionization is decreased, then the electrostatic constrain is diminished which in turn allows the chain segment to move more freely. Moreover, as shear rate is increased this
electrostatic constrain is overlaped by the energy imput on
the system, forcing the individual chain to flow. This phe-
nomenon clearly shows the importance of the repulsive
electrostatic forces in the network formation, as well as,
the role of shear in the reorientation process of the chains
in the "network". The significance of the electrostatic
interactions on the viscoelastic properties of polyelectro-
lytes in solution has been shown to be of paramount impor-
tance even in the dilute region. Electrostatic interactions
has been reported to be responsible for deviations from the
theoretical relationship at long relaxation times in both
polyglutamic acid and polyacrylic acid (Okamoto et al.,
1974; Nakajima and Wada, 1974).

From the region of times of relaxation where the
viscoelastic response is due to single strand motion, in
other words, where \( H \) is proportional to \( \tau^{-1/2} \), the monomeric
friction coefficient \( (\zeta_0) \) may be estimated. The monomeric
friction coefficient represents the frictional force per
monomer per unit velocity encountered by a submolecule junc-
tion as it moves through the medium. The coefficient \( (\zeta_0) \) is
calculated by the expression: (Rouse, 1953)

\[
H = \frac{a}{2} \frac{\rho}{\pi} \frac{N_0}{M_0} \left[ \frac{\zeta_0 K T}{6} \right]^{1/2} \tau^{-1/2}
\]

where:
a = diameter of chitosan monomer unit, 5.33 Å (Sklyar et al., 1981)
ρ = polymer concentration
N_0 = Avogadro's number
K = Boltzmann constant
T = absolute temperature
M_0 = monomer molecular weight

Values of the logarithm of ξ_0 are presented on Table 3. ξ_0 decreases markedly with dilution, nearly three orders of magnitude when chitosan concentration is decreased from 3.0 g/dl to 1.5 g/dl. This strong dependence of the friction coefficient on chitosan concentration may be due to the increase in the overlapping parameter with concentration. This result agrees with the increase in the modulus of entanglement with concentration previously discussed. Table 3 also indicates that ξ_0 is nearly unaffected by pH and ionic strength, for a given polymer concentration, which is in agreement with the results on the effect of shear on G', G" and η*. 
Table 3

Logarithm of the Monomeric Friction Coefficient ($\zeta_0^*$) for Concentrated Chitosan Solutions

<table>
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<tr>
<th>[Cl⁻] (M)</th>
<th>Chitosan (g/dl)</th>
<th>3.0</th>
<th>4.0</th>
<th>4.5</th>
<th>5.0</th>
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<td>-8.15</td>
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<td>-8.93</td>
<td>-8.66</td>
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<tr>
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<td>-9.81</td>
<td>-9.65</td>
</tr>
<tr>
<td>0.21</td>
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<td>-7.81</td>
<td>-7.79</td>
<td>-7.59</td>
</tr>
<tr>
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<td>-8.35</td>
<td>-8.19</td>
<td>-7.99</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>-9.12</td>
<td>-8.93</td>
<td>-8.94</td>
<td>-8.70</td>
</tr>
<tr>
<td></td>
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<td>-9.96</td>
<td>-10.09</td>
<td>-9.93</td>
</tr>
<tr>
<td>0.25</td>
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<td>-9.00</td>
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<tr>
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<tr>
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<td>-9.71</td>
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<td>-9.61</td>
</tr>
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</table>

*in (dyne - $\frac{sec}{cm}$)
VI. CONCLUSIONS

The following conclusions have been obtained as a result of this study:

1. Chitosan solutions (1.5 g/dl to 3.0 g/dl) are shear thinning at shear rates between 50 sec\(^{-1}\) to 3300 sec\(^{-1}\). The degree of pseudoplasticity is increased with the concentration of chitosan but unaffected by the pH and ionic strength of the solution.

2. Values of the modulus of the complex viscosity ranged from approximately 10 poises (1.5 g/dl chitosan concentration, pH=3.0, Cl\(^-\)=0.25) to 500 poises (3.0 g/dl chitosan concentration, pH=5.0, Cl\(^-\)=0.20) at low shear rates.

3. Both \(G'\) and \(G''\) increase with frequency (\(\omega=50\) sec\(^{-1}\) to \(\omega=3300\) sec\(^{-1}\)).

4. At chitosan concentrations greater than 2.5 g/dl, the imaginary component of the complex viscosity (\(\eta''\)) crossover the real component (\(\eta'\)), indicating a "gel-like" structure. The gel-like structure caused by the increase in chitosan concentration and pH no longer exist at shear rate above 1300 sec\(^{-1}\).
5. The master curve obtained when $J'(\omega)$ and $J''(\omega)$ were plotted against $G'(\omega)$ and $G''(\omega)$ respectively, indicates that the relaxation mechanism is unaltered by either chitosan concentration, pH and/or ionic strength.

6. The modulus of entanglement ($G_{en}$) increases from approximately $1.3 \times 10^3$ dyne/cm$^2$ to $1.8 \times 10^3$ dyne/cm$^2$ for 3.0 g/dl chitosan solution when pH is varied from 3.0 to 5.0. However, for polymer concentrations below 2.5 g/dl, $G_{en}$ is not a strong function of pH.

7. The entanglement coupling is highly dependent on polymer concentration. $G_{en}$ ranged from approximately $1.5 \times 10^2$ dyne/cm$^2$ for 1.5 g/dl chitosan solution to $1.3 \times 10^3 - 1.8 \times 10^3$ dyne/cm$^2$ for 3.0 g/dl solutions. However, $G_{en}$ was independent of ionic strength ($I = 0.2$ M to 0.3 M).

8. The logarithm of the relaxation spectrum function and the time of relaxation, when plotted, gave the slope of -0.5 for short and -1.0 for longer times of relaxation. This suggests that at short times single strand motions are responsible for the relaxation mechanism, and at longer time frames, the relaxation mechanism involve overall motions which extend over larger portions of the system.

9. The monomeric friction coefficient, calculated at short time of relaxation, is strongly concentration depen-
dent varying from approximately $5 \times 10^{-11}$ dyne-sec/cm for 1.5 g/dl chitosan solutions to nearly $3 \times 10^{-8}$ dyne-sec/cm for 3.0 g/dl solutions. Nevertheless, the friction coefficient is neither a function of the pH and ionic strength.
VII. SUGGESTIONS FOR FUTURE RESEARCH

Following study will aid to the further understanding of the solution behavior of chitosan.

a) Effect of the degree of ionization and chitosan concentration on the shear viscosity and first normal stress difference of concentrated chitosan solutions.

b) Effect of temperature on the rheological properties of concentrated chitosan solutions. This experiment would provide the activation energy of the junctions responsible for the pseudoplastic behavior of the concentrated chitosan solutions.
REFERENCES


Osaki, K., and J.L. Schrag. 1971. Viscoelastic Properties of polymer Solution in high-Viscosity Solvents and


BIOGRAPHIC NOTE