Rheological properties of chitosan solutions

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Abstract

Rheological properties of chitosan solutions were investigated as a function of polymer concentration. The viscosity curves for chitosan solutions consisted of two distinct viscosity regions, the Newtonian zero-shear viscosity (η_o) region and the shear rate dependent apparent viscosity (η_{app}) region. The shear rate dependence of viscosity was more clearly observed at higher chitosan concentrations. The critical coil overlap parameter ($C^*[\eta]$) was determined to be approximately 3.2 from a plot of zero-shear specific viscosity ($\eta_{sp,o}$) vs coil overlap parameter ($C[\eta]$), which was lower than $C[\eta]$ 4.0 reported for other random coil polysaccharides. It was also found that the slope of $\eta_{sp,o}$ vs $C[\eta]$ was 3.9 at concentrated $C[\eta]>C^*[\eta]$ domain, while 1.2 at dilute $C[\eta]<C^*[\eta]$ domain. The steady viscosity (η) of chitosan solution displayed a good superposition at η/η_o vs $\dot{\gamma}/\dot{\gamma}_{0.8}$ relation.

Keywords : chitosan, rheology, viscosity, coil overlap parameter

1. Introduction

Chitosan is a deacetylated derivatives of chitin consisting of β-1,4-N-acetylglucosamine (Varum *et al.,* 1994). Chitin is a plentiful biomass, which is widely distributed in nature as the skeletal structure of crustaceans, insects, mushrooms, and the cell wall of fungi (Knorr, 1984; 1991). Transformation of this unused biomass could be advantageous, since chitin and chitosan derivatives have numerous applications in the industry (Hirano *et al.,* 1987).

Chitosan is commercially manufactured from chitin (poly-β-(1,4)-N-acetyl -D-glucosamin) by heterogeneous alkaline deacetylation using concentrated NaOH solutions (Varum *et al.,* 1994; Muzzarelli, 1990). Chitosan, β-1,4 linked linear polymer of 2-acetamide-2-deoxy-β-D-glucose, is one of polysaccharides having a amino group instead of a hydroxyl group on the C2 position of the glucose residue of cellulose. Although chitosan bears a similar structure to cellulose, it contains, in addition to hydroxyl groups, acetylamine or free amino groups which make it very different in many properties from cellulose.

Chitosan is distinguished from chitin by its solubility in dilute aqueous acid solutions. Chitosan is positively charged due to amino groups at acidic pH, whose magnitude is dependent on the degree of deacetylation, and it

is thus classified as cationic polyelectrolytes (Peter, 1995). Chitosan is in reality the only cationic polysaccharide abundantly occurring in nature, while a majority of other polysaccharides confer either neutral or anionic charge. The versatile functions of chitosan reported have been ascribed to this cationic nature (Muzzarelli, 1996).

For the last two decades, chitosan and its derivatives have drawn considerable attention for its biological properties and potential uses in medical, food industrial, and agricultural fields (Li *et al.,* 1997). Chitosan possesses a variety of biological activities such as phytoalexin elicitor activity, host-associated antitumor activity, activation of immune response, anticancer activity, cholesterol lowering activity, antihypertension activity, antifungal activity, antibacterial activity, etc (Suzuli *et al.,* 1985; Nishimura *et al.,* 1984; Allan *et al.,* 1984).

In comparison with food and biological studies, the rheological properties of concentrated solutions are scarcely investigated to date, although a few reports have been published for the properties of dilute solution of chitosans (Hwang *et al.,* 1997; Roberts and Domszy, 1982). Polymers exist as an intermolecular entangled state in concentrated domain, in which accurate rheological characterization is of critical importance in terms of commercial processibility, physiological activity, product design, etc (Steffe, 1992). This research aims to investigate the concentration effects on the rheological properties of chitosan, particularly in the concentrated domain.

2. Experimental

2.1. Materials

Chitosan was prepared by alkaline deacetylation of chitin (No *et al.,* 1989). First, chitin was prepared by treating *Chitinonecetes opilio* with 3% HCl at 30°C for 3 hr (demineralization) and subsequently with 5% NaOH at 90°C for 12 hr (deproteinization). Then, chitin was treated with 40% NaOH at 70°C for 6 hr to remove the acetyl residues (deacetylation). The degree of deacetylation was determined to be 91% by the spectroscopic method using potassium polyvinyl sulfate (Kina *et al.,* 1974).

2.2. Intrinsic viscosity

The intrinsic viscosity of chitosan solution was measured by Cannon-Fenske glass capillary viscometer (Cannon Instrument Co., USA; size 50) at 25°C. A certain amount of chitosan was dissolved in 0.1 M NaCl/0.1 M CH₃COOH solution for 4 hr at room temperature. The chitosan solutions were filtered through a 0.45 μm Millipore filter to get rid of dusts and insoluble impurities. Then, 10 m*l* solution was pipetted into the capillary viscometer, which was equilibrated at 25°C water bath for 30 min prior to measurements. Intrinsic viscosity ([η]) were determined as follows:

$$[\eta] = \lim_{c \to 0} (\eta - \eta_s)/\eta_s C \tag{1}$$

where η is the solution viscosity, η_s is the solvent viscosity, and C is the solution concentration.

2.3. Shear viscosity

The shear viscosity was measured by Rheometrics Fluid Spectrometer (Rheometrics Inc., Piscataway, NJ, USA). A cone and plate geometry with a cone angle of 0.0196 radian and radius of 25 mm was used for the measurements, and the gap size was 50 microns. The shear rates ranged from 0.1 to 100 sec⁻¹ with 5 data points per log cycle. The experiments were conducted at 25°C. Steady-state shear viscosity is reported as a function of shear rate in log-log coordinates. Chitosan solutions for shear viscosity measurements were prepared by dissolving chitosans in 0.1 M NaCl/0.1 M CH₃COOH solution for 4 h at room temperature.

3. Results and discussion

As indicated in Eq. (1), when $(\eta-\eta_s)/\eta_s C$ is plotted vs concentration, the intercept corresponds to the intrinsic viscosity ([η]). Fig. 1 shows that the intrinsic viscosity of chitosan sample used in this research was 14.54 dl/g at 0.1 M NaCl/0.1 M CH₃COOH, whose molecular weight corresponds to approximately 1.71×10^6 on the basis of Mark-Houwink equation (Roberts and Domszy, 1982).
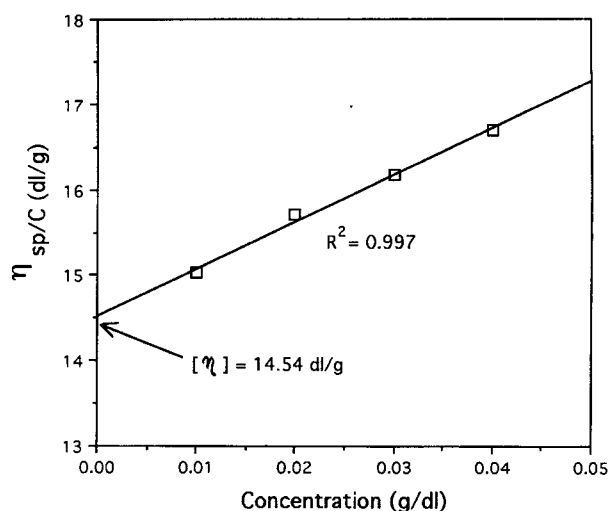

Fig. 1. Determination of intrinsic viscosity.

This magnitude of intrinsic viscosity of chitosan is higher than that of other biopolymers having the comparable molecular weight. It has been well documented that the cellulose based biopolymers confer the relatively higher intrinsic viscosity compared to other biopolymers of the similar molecular weight, ascribing to the more rigid conformation of β-(1,4) glucose linkages of cellulose (Smithrφd and Haug, 1971). As described previously, the backbone of chitosan is essentially composed of cellulose, which results in increasing the intrinsic viscosity of chitosan.

The shear rate dependence of viscosity is demonstrated in Fig. 2 in the concentration ranges of 0.25-2.5%. At first, two distinct viscosity regions are observed: the Newtonian flow region showing the constant zero-shear viscosity (η_o) at low shear rate and the power-law flow region showing

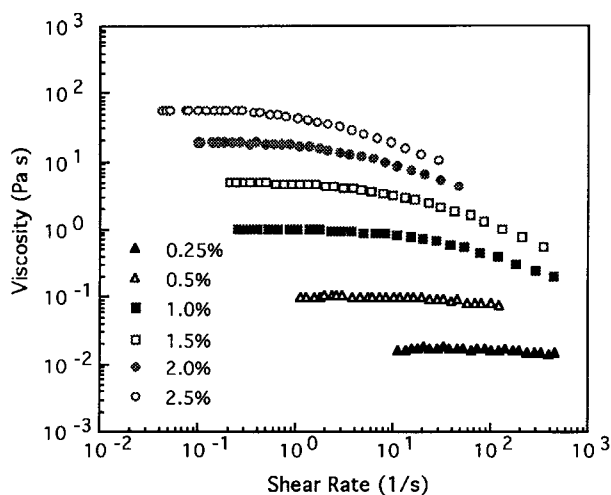
Fig. 2. Effect of concentration on the shear viscosity of chitosan solutions.

the shear rate dependent apparent viscosity (η_{app}) at relatively higher shear rate. At low shear rate, a constant zero-shear viscosity can be maintained, since the rate of intermolecular disentanglements brought about by shear force exerted is nearly the same as that of entanglements newly formed (Graessley, 1974). The zero-shear viscosity has been frequently employed to study the structure-function relation of biopolymeric systems (Hwang and Kokini, 1991). This is because the magnitude of zero-shear viscosity is a macroscopic representation of microstructural nature of biopolymers. In contrast, the viscosity decreases with increasing shear rates in the power-law region, since the rate of disentanglements is higher than that of entanglements (Graessley, 1974). The apparent viscosity determined in the power-law region confers practical information for the process optimization and sensory characterization of liquid foods (Morris, 1989).

It is apparent in Fig. 2 that increasing shear rate dependence of viscosity, i.e. more pseudoplastic, is observed with increasing chitosan concentration. This can be explained in terms of the degree of chain entanglements. As polymer concentration is increased, the freedom of movement of the individual chains becomes restricted due to the correspondingly increased number of entanglements (Graessley, 1974). This gives rise to an increase in time required to form new entanglements to replace those disrupted by the externally imposed deformation. Thus, the shear rate at which Newtonian behavior is lost progressively moves towards lower values with the increasing polymer concentrations. This is consistent with the report of Morris et al. (1981).

The shear thinning region η of vs $\dot{\gamma}$ curve can be expressed by the following power law or Ostward-De Waele equation (Nielsen, 1977):

$$\eta_a = K\dot{\gamma}^{n-1} \quad (2)$$

where η_a is the apparent viscosity, K is the consistency index, and n is the flow behavior index. As demonstrated in Fig. 3 for 2.0% chitosan solution, the transition flow region was clearly observed between the initial Newtonian region at the low shear rates and the final power law region at the higher shear rates. In most cases the intermediate transition flow region has been neglected for detailed characterization. However, it is thought that quantification of the transition region is also of rheological significance, since polymers can provide the distinct mechanisms in the early disentanglement stage, depending their molecular structure and interaction properties (Hwang, 1995).

The K and n values of chitosan obtained from the power region of η vs $\dot{\gamma}$ are presented in Table 1 as a function of concentration. The results indicate that the transition flow region can be also expressed in terms of the power law equation, and two distinct power flow regions, including the transition region, exist for chitosan solutions. The similar transition region, following the power-law flow, were also previously reported for citrus pectin solutions (Hwang, 1995). It is most probable that this phenomenon can be applied to a majority of polysaccharide solutions. Further detailed research is necessary as to how polysaccharides, possessing distinct structural features, respond differently

Table 1. Consistency (K) and flow behavior index (n) of chitosan solutions

Concentration (%)	log K_1	n_1	log K_2	n_2
2.5	1.645	0.698	1.789	0.472
2.0	1.264	0.701	1.462	0.497
1.5	0.852	0.720	1.088	0.507
1.0	0.450	0.746	0.575	0.520
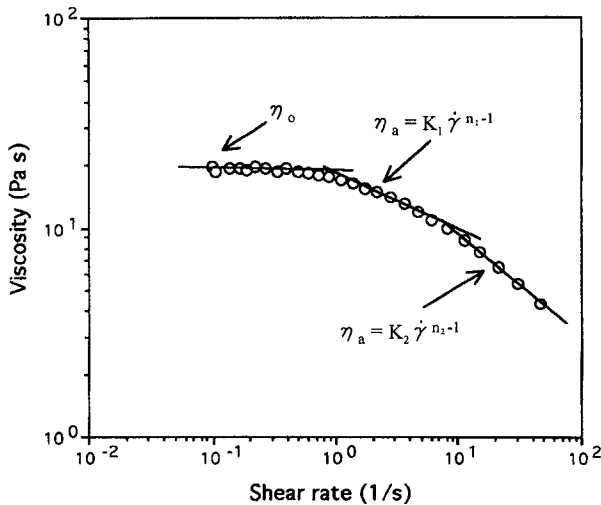
Fig. 3. The shear rate dependence of consistency (K) and flow behavior index (n) of 2% chitosan solution.
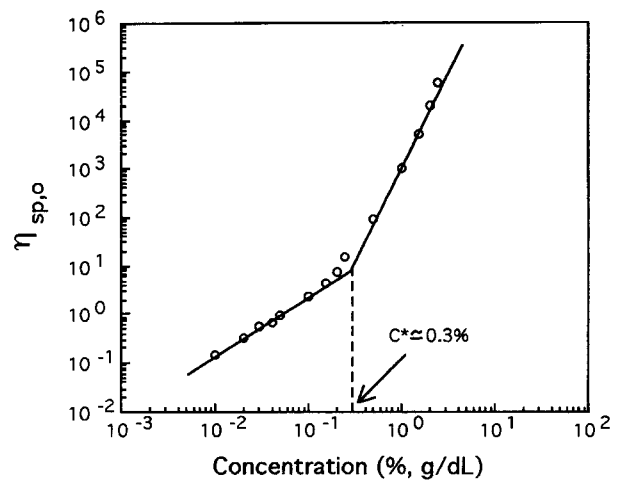
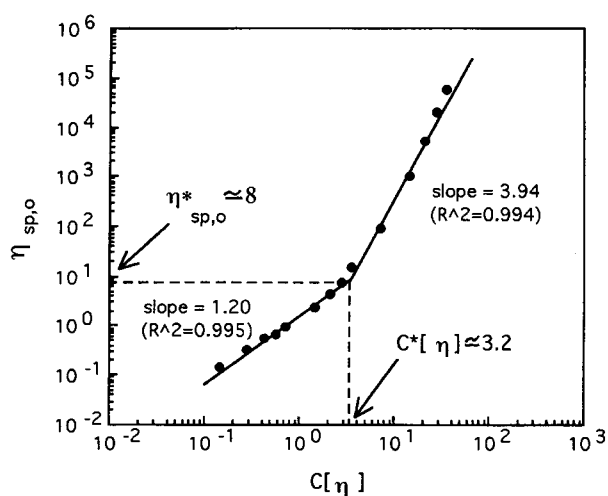Fig. 4. Effect of concentration on zero shear specific viscosity of chitosan solutions.

Fig. 5. $\eta_{sp,o}$ vs $c[\eta]$ of chitosan solutions.

Fig. 6. η/η_o vs $\dot{\gamma}/\dot{\gamma}_{0.8}$ of chitosan solutions.

at the initial disentangled state.

The concentration dependence of zero-shear specific viscosity ($\eta_{sp,o}$) is presented in Fig. 4, at which the critical concentration (C^*) represents a physical contact point of polymer. The figure shows that C^* was determined to be approximately 0.3% for chitosan used in this research. Intermolecular entanglements predominate the overall molecular motion of polymers at $C > C^*$, while individual molecules are statistically separated from other molecules at $C < C^*$. The critical concentration (C^*) is a measure of molecular size and conformation of a polymer: the higher molecular weight and the more rigid conformation, the lower C^*.

$\eta_{sp,o}$ vs C of a polymer varies depending on the molecular weight due to the corresponding changes in C^*. This can be generalized into a single plot by employing a dimensionless coil overlap parameter ($C[\eta]$). Fig. 5 shows the zero-shear specific viscosity ($\eta_{sp,o}$) vs the coil overlap parameter ($C[\eta]$) of chitosan used in this research. $C^*[\eta]$ of chitosan was approximately 3.2, which is somewhat lower than the report of Morris et al. (1981) that the onset of coil overlap for a variety of random-coil polysaccharides occurred when $C[\eta] \approx 4.0$. Fig. 5 also shows $\eta_{sp,o} \approx 8.0$ at the intersection point. In contrast, Morris and co-workers (1981) reported $\eta_{sp,o} \approx 10$ at the intersection point for other random-coil polysaccharides. Smithrϕd and Haug (1971) demonstrated that the rigid polymer can be more efficiently packed. Accordingly, the lower $C^*[\eta]$ and $\eta_{sp,o}$ at $C^*[\eta]$ may be attributable to the rigid conformation of cellulose-based chitosan structure.

Fig. 5 also shows that the slope of double logarithmic $\eta_{sp,o}$ vs $C[\eta]$ plot for chitosan was 1.2 in the dilute region ($C[\eta] < C^*[\eta]$). The gradients in the dilute domain are in fairly good agreement with the range of 1.1-1.4 for other polysaccharide, as reviewed by Launay et al. (1986). Mor-
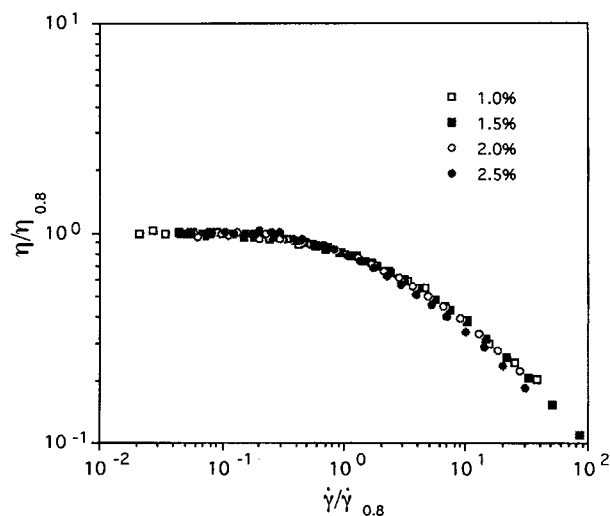
ris and co-workers (1981) also reported that the gradient of various random-coil polysaccharides studied were proportional to $\sim C^{1.3}$ at $C[\eta] < C^*[\eta]$. The gradients in dilute solutions are almost independent of the degree of branching and the intrinsic viscosity. These results are not surprising, because the flow parameters in dilute solutions are directly related to the hydrodynamic volume of the molecule, which is taken into account by the terms $C[\eta]$. In contrast, as shown in Fig. 3, the slope was 3.94 in the concentrated region ($C[\eta] > C^*[\eta]$). The slope approximated to be 3.4 for a majority of random-coil polysaccharides with an exception of galactomannans showing 5.1 (Morris et al., 1981; Launay et al., 1986).

Superposition of viscosity vs shear rate data obtained at different concentrations can be obtained, when the shear rate is multiplied by the time constant $\lambda_{0.8}$ or correspondingly $\dot{\gamma}_{0.8}$ at which η_o is reduced to $0.8\eta_o$ (Graessley, 1974). Thus, the shear-rate dependence of viscosity (Fig. 2) was replotted in Fig. 6 with respect to η/η_o vs $\dot{\gamma}/\dot{\gamma}_{0.8}$ curves. The result demonstrated that the viscosity of chitosan solution was closely superimposable for all concentrations studied. The similar observations were also report for other random-coil polysaccharides (Morris et al., 1981; Hwang and Kokini, 1992).

Acknowledgement

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