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Linear and nonlinear rheological responses in aqueous systems of hydrophobically modified chitosan and its unmodified analogue

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Summary

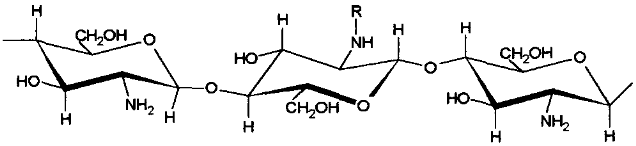
Oscillatory shear and viscosity measurements have been carried out on semidilute acid aqueous systems of unmodified chitosan (UM-chitosan) and of hydrophobically modified chitosan (HM-chitosan) with three different degrees of C12-aldehyde substitution. These systems form physical gels at higher concentrations. The gel point, determined by the observation of a frequency independent loss tangent, was found to be shifted toward lower concentrations with increasing hydrophobicity. At the gel point, a power law frequency dependence of the dynamic moduli ($G' \sim G'' \sim \omega^n$) was observed, with n values of 0.36 and 0.46 for the UM-chitosan and the hydrophobically modified chitosans, respectively. These values are interpreted in the framework of a fractal model. The gel strength parameter S increased with decreasing hydrophobicity. The UM-chitosan and HM-chitosan systems exhibited a non-Newtonian shear thinning behavior. This effect is promoted by increasing polymer concentration and hydrophobicity. Both the linear and nonlinear rheological properties elucidate the intricate interplay between hydrophobic associations and entanglement effects.

Introduction

Chitosan belongs to a family of linear, cationic biopolymers obtained from N-deacetylation of chitin in alkaline media. This polysaccharide is a random copolymer, containing (1→4) linked 2-acetamide-2-deoxy-β-D-glucopyranose and 2-amino-2-deoxy-β-D-glucopyranose residues. Chitosan is water-soluble at an acidic pH and has numerous applications in industry, pharmacy, and biotechnology (1).

Hydrogels of chitosan are of interest for various applications, particularly in the field of pharmacy or biomaterials, because chitosan possesses good biocompatibility and bioresorption properties. In most of the previous studies, the chitosan gels were chemically cross-linked by utilizing different cross-linking techniques (2-9). The rheological behavior of gelling chitosan systems under various conditions has been studied extensively (4,7,9-14). The influence of different parameters such as the type and concentration of cross-linking agent (6,7,9), cosolvent, concentration and molecular weight of chitosan (4,6,8-10), degree of deacetylation (4,7-9), pH (5,9,12), and the temperature (6,13) on the gelation process has been reported.

The non-Newtonian shear thinning behavior of chitosan systems has attracted a great deal of interest (10,12,15-19) in the last few years. The magnitude of this effect depends on factors such as molecular weight and concentration of chitosan, degree of deacetylation, surfactant addition, pH, and temperature.



Chitosan: R = H or R = -CO-CH_3
HM-chitosan: R = H or R = C12-aldehyde or R = -CO-CH_3

Fig. 1. A schematic illustration of the structure of unmodified chitosan and the hydrophobically modified chitosan

In the present work, we have examined linear and nonlinear viscoelasticity of acid aqueous systems of unmodified chitosan (UM-chitosan) and of hydrophobically modified chitosan (HM-chitosan) with three different degrees of hydrophobicity. The HM-chitosan consists of C12-aldehyde chains grafted to the polymer backbone. An illustration of the structure of chitosan is depicted in Fig. 1. Above a certain value of the polymer concentration, this type of system exhibits a concentration-induced gel-like state (10) due to specific molecular interactions and physical entanglements. With the aid of oscillatory shear experiments, we have determined the gel point concentration for the chitosan systems, and this concentration was found to decrease with increasing degree of hydrophobicity of the polymer. Furthermore, the shear rate dependence of the viscosity of the UM-chitosan and HM-chitosan systems was examined. The results reveal that the feature of non-Newtonian shear-thinning behavior depends on the polymer concentration and the degree of hydrophobicity of the polymer. The principal objective of this work is to obtain a better understanding of how the concentration and the hydrophobicity of the polymer affect the linear and nonlinear rheological responses in this type of systems.

Experimental section

The unmodified chitosan sample was obtained from Pronova Biopolymers (Drammen, Norway). The degree of N-deacetylation was determined to be 84 % by ^{1}H-NMR spectroscopy (20). By using low-angle laser light scattering and size-exclusion chromatography, the weight-average molecular weight was found to be M_w=4 x 10^5 and the polydispersity index was M_w/M_n=2.7. The details of these methods in the characterization of chitosans have been reported elsewhere (21). The hydrophobically modified chitosans are equivalent to the unmodified chitosan sample but with C12-aldehyde chains grafted to the polymer backbone. These samples were prepared by reaction with the amino groups on the polymer chains with a C12-aldehyde. The procedure employed here is similar to that described previously (22). In this investigation, the degrees of C12-aldehyde substitution were 2.5, 5, and 10 mol %. Aqueous samples of chitosan and HM-chitosan in 1% acetic acid were prepared by weighing the components, and the samples were homogenized by standing at room temperature for three days. All the measurements were carried out at 25 °C. At these conditions pH ≅ 3.5.

Oscillatory shear and viscosity experiments were conducted in a Bohlin VOR rheometer system using, depending on the viscosity of the sample, a double-gap concentric cylinder, an ordinary concentric cylinder geometry, or a cone-and-plate geometry, with a cone angle of 5° and a diameter of 30 mm. The double-gap device is applicable for low-viscosity liquids. The oscillatory shear measurements were performed within the linear viscoelastic regime, where the storage (G') and loss (G") moduli are independent of the strain amplitude. The viscosity measurements were carried out over an extended shear rate range.

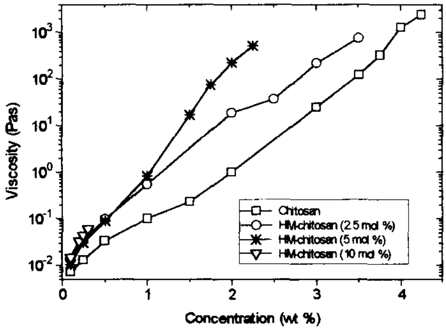


Fig. 2. Concentration dependence of the viscosity (all the data have been collected in the zero-shear-rate Newtonian plateau) of semidilute acid aqueous solutions of chitosan of different degrees of hydrophobicity.

Results and discussion

Linear viscoelasticity

Table 1. Characteristic data for incipient chitosan and HM-chitosan gels.

Hydrophobicity (mol %)	$c^* = 1/[\eta]$ (wt %)	Gel concentration (wt %)	n	S (Pas^n) (calculated from eq. 2)	d_f (calculated from eq. 1)
0	0.044	3.9	0.36	232	2.2
2.5	0.024	3.0	0.46	83	2.0
5.0	0.027	1.7_5	0.46	24	2.0

The effect of hydrophobic substitution is illustrated in Fig. 2, where the viscosity at a low shear rate (in the zero-shear-rate Newtonian plateau) is plotted as a function of polymer concentration for systems of unmodified chitosan and of hydrophobically modified chitosans in 1 % acetic acid. It is obvious that the viscosity raises with increasing polymer concentration and that this increase is stronger as the hydrophobicity of the polymer increases. The hydrophobic association effect on the viscosity becomes gradually more marked as the polymer concentration increases. The rather restricted concentration range covered by the most hydrophobic sample (10 mol

%) is due to the fact that this HM-chitosan cannot be dissolved in this solvent above a polymer concentration of 0.3 wt %. We should note that even for the UM-chitosan there is a pronounced increase in the viscosity at high concentrations. In the high concentration regime, it is likely that the entanglement effect will play an important role in the viscosity process. However, in a recent fluorescence study (23) on an unmodified chitosan sample, enhanced intermolecular hydrophobic interactions were observed with increasing polymer concentration. All the rheological measurements in this study have been carried out in the semidilute concentration regime, where intermolecular associations are expected to prevail. The onset of this regime can be estimated from the overlap concentration $c^*=1/[\eta]$, where $[\eta]$ is the intrinsic viscosity. From intrinsic viscosity data (24) for the UM-chitosan and HM-chitosan systems, the values of c^* have been determined and collected in Table 1. These low values reveal that the concentrations considered in this study are well in the semidilute range.

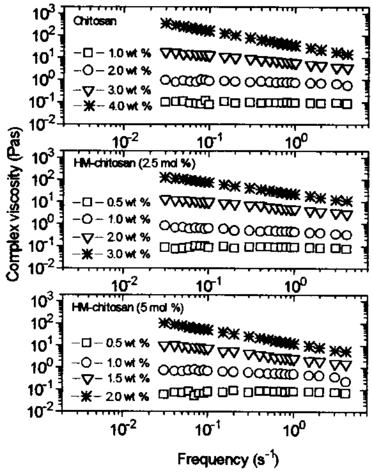


Fig. 3. Plots of the effect of the frequency of oscillation on the complex viscosity of unmodified and hydrophobically modified chitosans at the conditions indicated

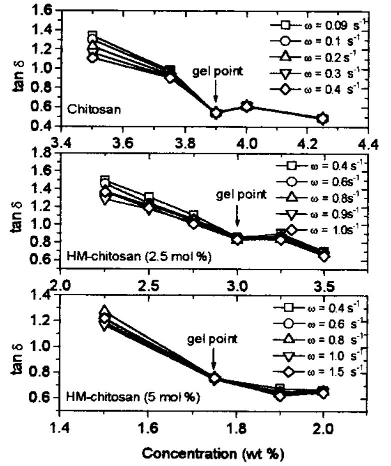


Fig. 4. Viscoelastic loss tangent as a function of polymer concentration for the systems and frequencies indicated

The effect of the frequency of oscillation on the complex viscosity η^* ($\eta^* = (G'^2 + G''^2)^{1/2}/(2\pi\cdot\text{freq.})$) of systems of UM-chitosan and HM-chitosans is depicted in Fig. 3. At low concentrations the systems exhibit liquid-like behavior, i.e. η^* is practically independent of frequency. However, as the concentration and the degree of hydrophobicity increase the results indicate that the polymer systems become more viscoelastic, i.e. displaying enhanced frequency dependence of η^*, typical of polymer network systems containing cross-linked or entangled chain networks. We can see that both the concentration and the degree of hydrophobic modification contribute to the increased frequency dependence of η^*.

The concentration-induced gel point can be determined by observation of a frequency-independent value of tan δ (tan δ = G''/G', where δ is the phase angle) obtained from a multifrequency plot of tan δ versus polymer concentration. This type of plot is shown in Fig. 4 for systems of UM-chitosan and HM-chitosans. The general trend is similar for all the systems: a steady decrease in the loss tangent, with the decrease most pronounced for the lowest measurement frequency. This results in values of tan δ becoming frequency independent at a certain gelation concentration, which is dependent on the degree of hydrophobicity of the polymer. The gel concentrations obtained by this procedure are in good agreement with those observed with the test tube "tilting" method (25), where the gelation concentration was determined by tilting the test tube containing the solution. In this approach the concentration at which the solution no longer flows is taken as the concentration of gelation. It is evident from Fig. 4 that the gel point concentration decreases with increasing degree of hydrophobicity of the polymer (see also Table 1). This suggests that the hydrophobic interactions play an important role in the gelation process.

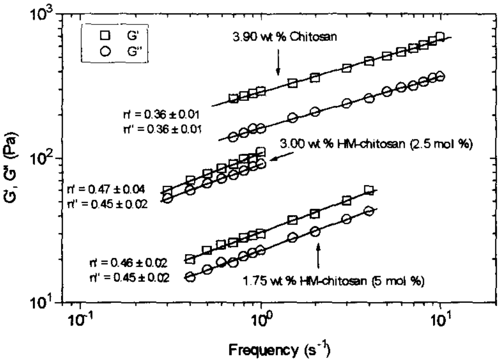


Fig. 5. Plot of G and G versus frequency for the indicated systems at the gel point, showing the power law behavior

At the gel point, G' and G" curves become parallel to each other, and the power law behavior ($G' \sim G'' \sim \omega^n$) in frequency is observed (see Fig. 5). The value of the viscoelastic exponent is practically the same for the HM-chitosans but somewhat smaller for the system of UM-chitosan (see Table 1). This may be due to stronger entanglement couplings for the UM-chitosan system. It has been argued (26) that an increasing entanglement density may give rise to lower values of n.

The values of n observed for these systems are considerably smaller than that (0.7) predicted for percolating networks (27,28). To rationalize values deviating from the percolation value, Muthukumar (29) developed a theoretical model in which it is assumed that the variations in the strand length between cross-linking points of the incipient gel network gives rise to changes in the excluded volume interactions. The surmise is that increasing strand length will enhance the excluded volume effect. If the excluded volume interaction is fully screened, the relaxation exponent for a polydisperse system may be written as (29)

$$n = d(d+2-2d_f)/2(d+2-d_f) \qquad (1)$$

where d (d=3) is the spatial dimension and d_f is the fractal dimension which relates the mass of a molecular cluster to its radius of gyration by $R^{d_f} \sim M$. In the framework of eq. (1), all the values of the exponent $0<n<1$ are possible for a fractal in the physically realizable domain $1 \leq d_f \leq 3$. The value of the fractal dimension, calculated with the aid of eq. (1), for the UM-chitosan is higher than those of the hydrophobically modified chitosans (see Table 1). This finding indicates (29,30) that the incipient network of the UM-chitosan is more "tight" than those of the HM-chitosans. In this context we should note the previous intrinsic viscosity results (24) on the same polymers, suggest that the molecules of UM-chitosan are more compact than those of the HM-chitosans. It is possible that the introduction of hydrophobic groups produce a gel structure with some branches, giving rise to a more "open" network structure. We should note that these values of d_f are significantly higher than that (1.3) observed (31) from a small-angle x-ray scattering study on a solution of chitosan (with a degree of deacetylation of 79 %) in 2 wt % acetic acid aqueous solution. The reason for this difference in fractal dimension is not clear, but it was found that the heterogeneous structure was very sensitive to the degree of deacetylation of the chitosan sample.

The viscoelasticity of an incipient gel can be characterized by the gel strength parameter S (32), which depends on the cross-linking density and the molecular chain flexibility. This material parameter can be defined with the aid of the following expression (32)

$$G' = S\,\omega^n\,\Gamma(1-n)\cos\delta \qquad (2)$$

where $\Gamma(1-n)$ is the gamma function. It is evident from Table 1 that S increases with decreasing degree of hydrophobic substitution. This observation suggests that the entanglement couplings are more effective in the cross-linking process of the gel network than the specific interactions in form of hydrophobic associations.

Nonlinear viscoelasticity

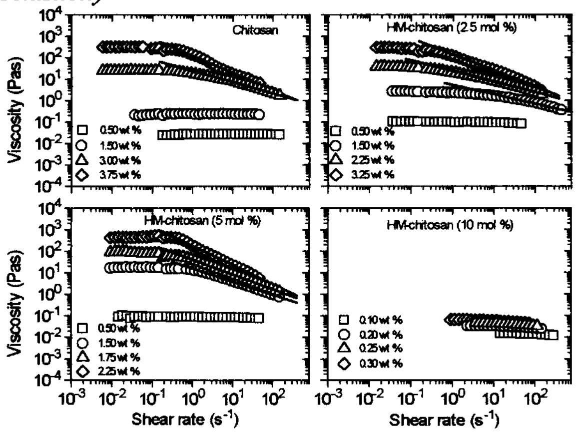


Fig. 6. Shear rate dependence of the viscosity for the concentrations and systems indicated

A typical feature of associating polymers is a strong shear dependence of the viscosity. Fig. 6 shows the effect of shear rate on the measured viscosity for the unmodified and hydrophobically modified chitosans at different concentrations. We observe shear-thinning behavior at higher shear rates, and this effect is strengthened with increasing polymer concentration and hydrophobicity. At low concentrations, the systems exhibit Newtonian behavior, but as the concentration raises the feature of non-Newtonian shear-thinning is first visible for the most hydrophobically modified polymer. The observation that the shear-thinning effect becomes stronger as the concentration increases has already been reported (10,16,19) for different chitosan systems. The decrease in the viscosity with increasing shear rate can be attributed to the disruption of the network junctions; that is, the rate of junction disruption exceeds the rate at which hydrophobic associations can be re-formed. In this context it should be mentioned that no disturbing hysterises effects (33,34) were observed when the shear rate was first increased and then decreased back to its initial value.

The relative degree of shear thinning exhibited by the UM-chitosan and HM-chitosan systems can be quantified by application of a simple power law relationship, which may be expressed as

$$\eta \sim \dot{\gamma}^{(\alpha-1)} \qquad (3)$$

where $\dot{\gamma}$ is the shear rate and α is the power law index. The values of the power law exponent of the shear-thinning sections of the curves illustrated in Fig. 6 are given in Table 2. These results reveal that both increasing polymer concentration and hydrophobicity promote the shear-thinning effect at elevated shear rate.

Table 2. Values of the characteristic exponent (α) describing the non-Newtonian behavior of chitosan and the HM-chitosans.

Hydrophobicity (mol %)	Polymer concentration (wt %)	α (see eq. 3)
0	3.00	0.47
	3.75	0.20
2.5	1.50	0.56
	2.25	0.50
	3.25	0.25
5.0	1.50	0.39
	1.75	0.31
	2.25	0.11

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