Polymer Bulletin 38, 71–79 (1997)

Polymer Bulletin

Effect of surfactant concentration, pH, and shear rate on the rheological properties of aqueous systems of a hydrophobically modified chitosan and its unmodified analogue

Anna-Lena Kjøniksen[1], **Bo Nyström**[1], **Torgeir Nakken**[2], **Odd Palmgren**[2], **Terje Tande**[2]

[1] Department of Chemistry, University of Oslo, P.O. Box 1033, Blindern, N-0315, Oslo, Norway
[2] Norsk Hydro, Research Centre Porsgrunn, Department of Polymer and Surface Chemistry, P.O. Box 2560, N-3901, Porsgrunn, Norway

Received: 25 September 1996/Revised version: 30 October 1996/Accepted: 4 November 1996

Summary

Oscillatory shear, shear relaxation and viscosity experiments have been carried out on semidilute solutions of chitosan and on a hydrophobically modified analogue (HM-chitosan) in 1 % acetic acid. This was done in the presence of various amounts of cetyltrimethylammonium bromide (CTAB) and at different pH values. All the rheological measurements on the HM-chitosan solutions revealed significant polymer-surfactant interaction and pH effects. The observed rheological effects were least pronounced at pH≈4, while a strong viscoelastic response was found at pH values of 1 and 5 in HM-chitosan solutions of low surfactant concentration. At these conditions, significant shear-thinning effects were observed. In semidilute solutions of unmodified chitosan, the influence of pH, surfactant concentration and shear rate on the rheological properties was moderate or insignificant.

Introduction

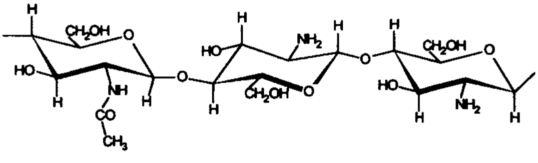


Fig. 1. Structure of chitosan

Chitosan is the name used for low acetyl forms of chitin and may be considered as a family of unbranched binary hetero-polysaccharides of β(1→4)-linked 2-acetamido-2-deoxy-β-D-glucopyranose and 2-amino-2-deoxy-β-D-glucopyranose of varying composition (1,2), see Fig. 1. The polymer chitosan has been considered for use as chelating agents for metals (3), flocculants, adhesives, adhesion for the food processing, paper and textile industries (4), membranes (5), and in cosmetic and biomedical applications (6). Chitosans having different degrees of deacetylation are produced from chitin by a deacetylation reaction, and can be dissolved in water under acidic conditions (1) by virtue of their polycationic nature. Due to the presence of protonated amino groups, chitosan in solution exhibits polyelectrolyte character and its dynamic behaviour in the solution is extremely complex, even in the absence of electrolyte (1,7). This biopolymer can be chemically modified (8,9) on the free amino groups or the hydroxyl groups present along the main chain to obtain a hydrophobically modified polymer.

It is known that the hydrodynamic and rheological behaviour of chitosan macromolecules in solution depends on factors such as polymer concentration, salinity, temperature, shear stress, surfactant concentration, pH of the solution, and the hydrophobicity of the polymer. In order to gain a more detailed insight into these phenomena, we have carried out rheological measurements on semidilute systems of chitosan and of a hydrophobically modified analogue (HM-chitosan) in the presence of various amounts of the cationic surfactant cetyltrimethylammonium bromide (CTAB) at different pH values. The aim of this study is to shed some light on the factors that govern the rheological behaviour in this type of systems. Most of the interest will be focused on differences between the unmodified chitosan and the modified chitosan.

Experimental

The unmodified chitosan sample was kindly provided by Pronova Biopolymers (Drammen, Norway). The N-deacetylation degree was determined to be 84 % by ^{1}H-NMR spectroscopy. Low angle laser light scattering (LALLS) and size-exclusion chromatography (SEC) experiments revealed a weight-average molecular weight of $M_w=4x10^5$ and a polydispersity index $M_w/M_n \approx 2.7$. The hydrophobically modified chitosan analogue was prepared by reaction with the amino groups on the polymer chain with a C12-aldehyde. In this study, a chitosan sample with a hydrophobic substitution degree of 5 mol % C12-aldehyde chains grafted to the polymer backbone was used. Semidilute chitosan systems of 1 wt % in aqueous solutions of 1 % acetic acid were prepared. The pH of the solutions was adjusted to the desired value by using HCl (aq) or KOH. The initial pH values of the chitosan solutions were around 4, and more acidic conditions were made by adding HCl (aq) and pH values above 4 were achieved by addition of KOH. The samples were prepared by weighing the components, and the solutions were homogenised by stirring at room temperature for several days. These solutions were found to be stable for at least 9 days at room temperature.

Oscillatory shear, stress relaxation and viscosity measurements 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 (C 25), or 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 and stress relaxation measurements were carried out within the linear viscoelastic region, where the storage (G') and lost (G'') moduli are independent of the strain amplitude. All measurements were performed at 25 °C on solutions with a constant polymer concentration of 1 wt %.

Results and discussion

In Fig. 2, results from the shear-flow viscosity measurements at a low frequency (1.5 Hz) are depicted for the systems chitosan (1 wt %)/CTAB and HM-chitosan (1 wt %)/CTAB as a function of surfactant concentration and at different pH values. This polymer concentration is well in the semidilute regime. The overlap concentration c^*, estimated from $c^*=1/[\eta]$, is found to be 0.05 wt %, where $[\eta]$ is measured in the presence of salt in order to avoid polyelectrolyte effects. It is clearly demonstrated that the complex viscosity η^* ($\eta^* = (G'^2 + G''^2)^{1/2}/(2\pi \cdot \text{freq.})$) is much higher for the hydrophobically modified chitosan, than for the unmodified analogue at all the considered pH values and surfactant concentrations. This suggests that the association network built up from the hydrophobically modified chitosan is much stronger than the corresponding one from the unmodified polymer. In this process, the chains of the HM-polymer are probably effectively cross-linked by the intermolecular association of neighbouring hydrophobic side chains. For the modified polymer, the complex viscosity passes through a flat maximum at a surfactant concentration of about 1 mmolal, which is close to the expected critical micelle concentration (cmc) of CTAB. This behaviour indicates enhanced polymer-surfactant interaction, and the general conjecture is that the formation of "mixed micelles", consisting of CTAB molecules and hydrophobic side chains of the polymer, increases the degree of interpolymer association and, consequently, the solution viscosity. We may note that a recent rheological study (10) on chitosan systems has revealed that also a nonionic surfactant gives rise to polymer-surfactant interactions. At higher CTAB concentration, the complex viscosity of HM-chitosan is observed to decrease and this trend is probably due to the "solubilisation" of the polymer-bound hydrophobes (11), and the average number of bound hydrophobes per surfactant aggregate is expected to decrease. As a result of this, the cross-links will untie, and the network structure will gradually breakdown as the surfactant addition increases. These effects are illustrated in Fig. 3. The type of behaviour of η^* displayed in Fig. 2 for the HM-chitosan systems, has previously been reported for other hydrophobically modified polymers, e.g. cellulose ether systems (11,12).

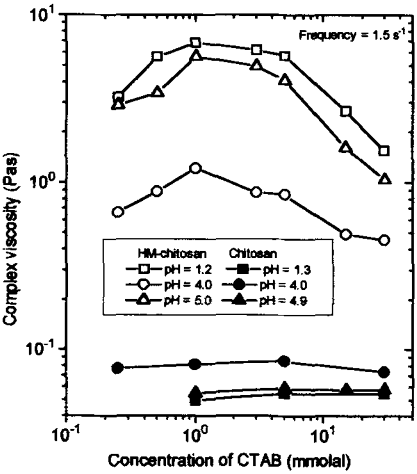
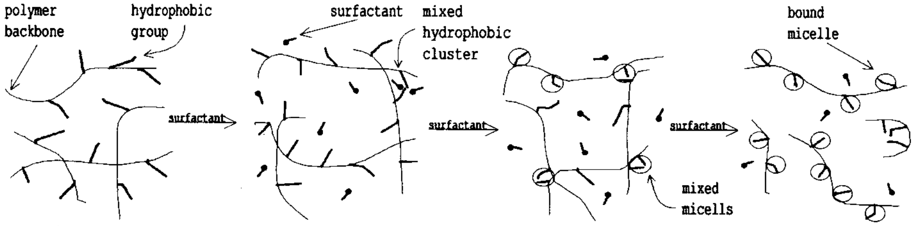


Fig. 2. Effect of pH and the addition of surfactant on the complex viscosity (η^*) (ω=1.5 Hz) of 1 wt % solutions of the systems indicated

The complex viscosity curves depicted in Fig. 2 for the HM-chitosan systems at different pH, exhibit a similar pattern of behaviour, but the value of η* is strongly influenced by the pH of the solution. The highest values of η* are observed at a low pH (pH=1.2) and η* decreases with increasing pH up to pH=4, and above this value η* increases again (see also Fig. 4). The complex viscosity of the unmodified chitosan is practically independent of surfactant concentration and there is only a moderate pH dependence of η*, with the highest values of η* at pH=4.



HM-chitosan solution without surfactant.

HM-chitosan solution in the presence of *low* surfactant concentration.

HM-chitosan solution in the presence of *moderate* surfactant concentration.

HM-chitosan solution in the presence of ***high*** surfactant concentration (disruption of the network).

Fig. 3. The addition of CTAB to the HM-chitosan solution results in an increased viscosity at low and moderate surfactant concentrations, where the surfactant binds the hydrophobic groups together. When the CTAB concentration is raised further, disruption of the network gradually occurs due to the formation of bound micelles.

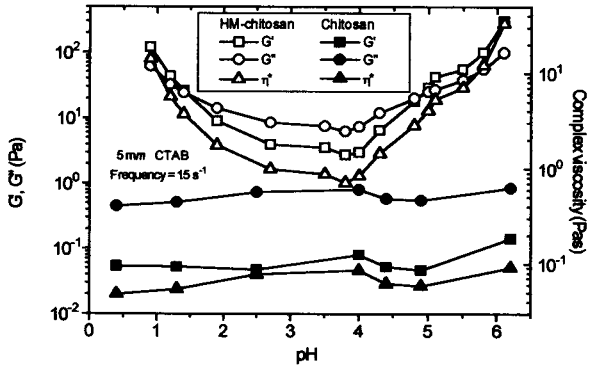


Fig. 4. Effect of pH on the complex viscosity (η*), storage (G′) and loss (G″) moduli (ω=1.5 Hz) of 1 wt % solutions of chitosan and HM-chitosan in the presence of 5 mmolal CTAB

At pH values around 4, most of the amino groups of chitosan are supposed to be protonated, and since increased protonation increases electrostatic repelling between charged groups of the same sign, it leads to enhanced swelling of the polymer network. By addition of base (KOH) to the initial chitosan solution, the value of pH increases above 4 and neutralisation of the excess acetic acid present in the chitosan solution occurs. As a result a completely dissociating salt is formed and consequently the ionic strength of the chitosan solution increases. At pH values above 4, the screening of the charges on the HM-chitosan chains will lead to poorer thermodynamic conditions and this will favour enhanced intermolecular hydrophobic contacts and hence the complex viscosity will increase. In the range $5.8 \leq pH < 6.4$, a gel zone evolves (at this stage the sample experiences no flow when a test tube is turned upside-down for a longer time) and at higher values of pH (the pK_a of chitosan is 6.3) phase separation occurs. In an analogous way, the ionic strength will increase when the initial chitosan solution is made more acid (pH<4; addition of HCl (aq)) and enhanced intermolecular hydrophobic association of the HM-chitosan is promoted. It should be mentioned that at pH≈0.7, a transparent gel is formed, while at pH below 0.5 incipient phase separation occurs.

The effect of pH on the complex viscosity and the dynamic moduli at constant frequency (1.5 s^{-1}) and at a surfactant concentration of 5 mmolal is illustrated in Fig. 4 for chitosan and HM-chitosan. We can see that the viscoelastic response increases at pH values below and above pH≈4 for the HM-chitosan system. For the unmodified chitosan, the effect of pH is weak. The same trends as those observed for HM-chitosan and chitosan in the presence of 5 mmolal CTAB are also detected in the presence of other surfactant concentrations (1-30 mmolal). These different features detected for HM-chitosan and chitosan suggest that the hydrophobic groups play a crucial role for the rheological properties.

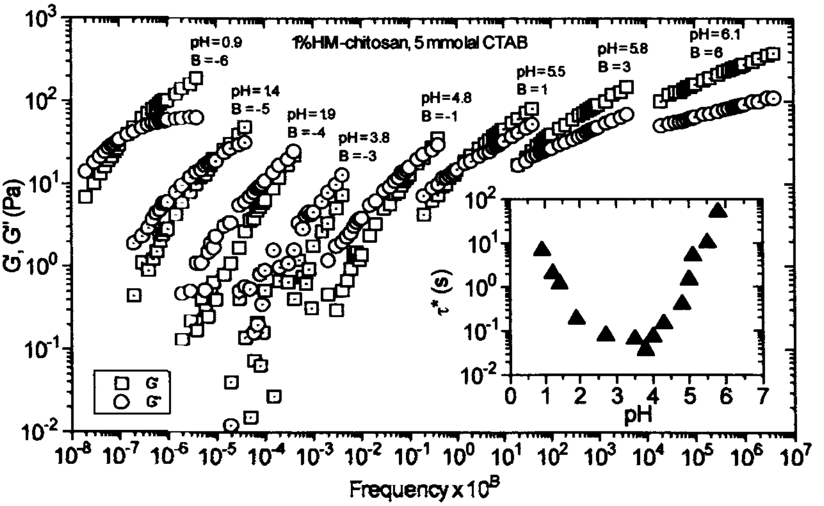


Fig. 5. Frequency dependencies of the storage modulus G′ and the loss modulus G″at different pH values of 1 wt % solutions of chitosan and HM-chitosan in the presence of 5 mmolal CTAB. The curves have been shifted horizontally by a factor 10^B of the value listed in the inset. The inset plot shows the pH dependence of the time of intersection τ* (see text)

Fig. 5 shows changes in the frequency dependence of G′ and G″ at different experimental conditions for 1 % HM-chitosan in 5 mmolal CTAB. In order to avoid overlap, the data are shifted horizontally by a factor 10^B of the value listed in the insert. The general trend is that at low frequencies, we observe a viscous behaviour with G″>G′, while at higher frequencies, depending on the value of pH, G′ increases to cross G″, and above this frequency, G′ exceeds G″, which suggests that the elastic response dominates. These results indicate that the polymer solutions become more elastic at higher frequencies, which is typical for networks containing entangled polymer chains. The lowest frequency of intersection is found at a pH around 4. At pH=6.1 (in the gel zone) G′>G″ over the frequency domain studied.

The frequency of intersection ω^* (G′=G″), may be determined from G′ and G″ data. In the inset plot of Fig. 5, the equivalent quantity, the time of intersection, τ^* ($\tau^*=1/\omega^*$), is plotted as a function of pH. This quantity can be regarded as a relaxation time for chain disengagement of the network. We may note that the value of τ^* is at its minimum at pH≈4 and increases toward lower and higher pH values. This increase of τ^* at "low" and "high" pH values is probably another manifestation of the strong hydrophobic associations operating at these pH values.

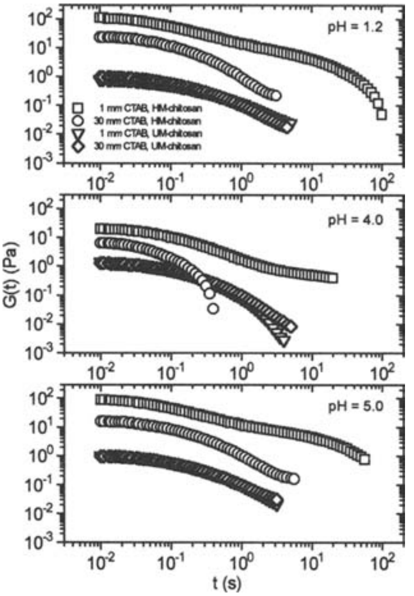


Fig. 6. Plot of the shear relaxation modulus G(t) versus time for the systems and pH values indicated

The decay of the linear relaxation modulus G(t) (determined from stress relaxation measurements) at different surfactant concentrations and pH values is shown in Fig. 6 for chitosan and HM-chitosan. The general trend for HM-chitosan at different pH conditions is that the decay times of the relaxation functions are shifted toward higher values when the surfactant concentration is low, and that G(t) is highest at the pH values of 1.2 and 5.0 in the presence of low CTAB concentration. These features, indicating enhanced elastic response, are consistent with those reported above from the other rheological experiments. In the case of the unmodified chitosan, no significant influence of pH or surfactant concentration on the stress relaxation function is revealed.

The effects of surfactant concentration and pH on the initial relaxation modulus G(0) (G(0) is taken as the value of G(t) for the lowest measured value of t) of 1 wt % solutions of chitosan and HM-chitosan are depicted in Fig. 7. These findings are very similar to those reported above from the oscillatory shear measurements (see the discussion in connection with Figs. 2 and 4). Again we can see the significant influence of surfactant concentration and pH on the viscoelastic properties of HM-chitosan, while no such effect is observed for the unmodified chitosan. This behaviour again stress the importance of the hydrophobic associations on the rheological properties.

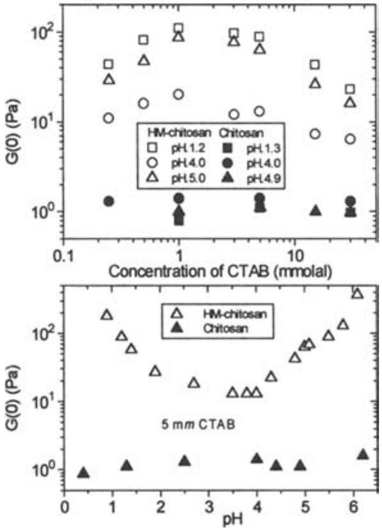


Fig. 7. Surfactant concentration and pH dependencies of the initial shear relaxation modulus G(0) for the systems indicated

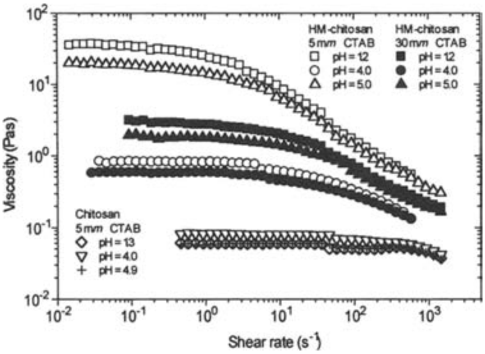


Fig. 8. Shear rate dependence on viscosity (η) for the systems and conditions indicated

The effect of shear rate ($\dot{\gamma}$) on the viscosity (η) is depicted in Fig. 8 for chitosan and HM-chitosan solutions at different experimental conditions. It is evident that the unmodified chitosan exhibits practically Newtonian flow behaviour at the various conditions studied and in the shear rate range examined. For the HM-chitosan, on the other hand, the shear rate dependence of the viscosity is significant. In this case, the shear-thinning effect is most pronounced at a low surfactant concentration (5 mmolal) in solutions of pH values of 1.2 and 5.0. The effect is less dominant at pH=4.0 and in solutions of high surfactant concentration (30 mmolal). These findings indicate that in chitosan systems where strong intermolecular interactions prevail, high shear rates will give rise to a disruption of the dynamic association network. Rheological studies (13-15) on various chitosan systems seem to indicate that high polymer concentrations and/or low degrees of deacetylation favour non-Newtonian behaviour.

In a recent rheological study (16) on chitosan systems it was found that the shear rate dependence on the viscosity could be described by a power law of the following form $\eta \sim \dot{\gamma}^{(1-n)}$. We can analyse our data in the high shear rate domain for the system HM-chitosan/5 mmolal CTAB at the pH values 1.2 and 5.0 by utilising this power law relationship (see Fig. 8). In this case a value of $n \approx 0.3$ is observed, which indicates a non-Newtonian nature of the solution. This value is somewhat lower than those reported for other modified chitosan systems (n=0.5-1) in ref. 16. It has been argued (16) that higher values of n are expected for polymers capable of strong self-association.

Acknowledgement

This work was supported by Norsk Hydro and the Norwegian Research Council through the program PROSMAT.

References

1. Muzzarelli RAA (1977) In: Muzzarelli RAA (ed.) Chitin, Pergamon Press, Oxford (p.1)
2. Jeuniaux C, Voss-Foucart M, Poulicek M, Bussers J (1989) Sources, Chemistry, Biochemistry, Physical Properties and Applications. In: Skjåk-Bræk G, Anthonsen T, Sandford P (eds.) Chitin and Chitosan, Elsevier Applied Science, London (p. 3)
3. Muzzarelli RAA, Tanfani F, Emanuelli M, Mariotti S (1982) Carbohydr. Res., 88: 172
4. Zikakais JP (ed.) (1984) Chitin, Chitosan and Related Enzymes, Academic Press Inc., New York
5. Nakatsuka S, Andrady AL (1992) J. Appl. Polym. Sci., 44: 17
6. Muzzarelli RAA (1989) In: Skjåk-Bræk G, Anthonsen T, Sandford P (eds.) Chitin and Chitosan, Elsevier Applied Science, London (p. 491)
7. Kienzle-Sterzer C, Rodrigues-Sanches D, Rha C (1982) J.Appl. Polym. Sci., 27: 4467
8. Moore GK, Roberts GAF (1982) Int. J. Biol. Macromol., 4: 246
9. Yalpani M, Hall LD (1984) Macromolecules, 17: 272
10. Jocic D, Julia MR, Erra P (1996) Colloid Polym. Sci., 274: 375

11. Tanaka R, Meadows J, Williams PA, Phillips GO (1992) Macromolecules, 25: 1304
12. Nyström B, Thuresson K, Lindman B (1995) Langmuir, 11: 1994
13. Delben F, Lapasin R, Pricl S (1990) Int. J. Biol. Macromol., 12: 9
14. Chen R-H, Lin W-C (1992) J. Fish. Soc. Taiwan, 19: 299
15. Nudga LA, Bochek AM, Kallistov OV, Kuchinskii SA, Petropavlovskii GA (1993) Zhurnal Prikladnoi Khimii, 66: 198
16. Holme KR, Hall LD, Speers RA, Tung MA (1992) Carbohydr. Res., 225: 307