Dynamic Rheological Properties of Concentrated Chitosan Soltions

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Abstract:
A detailed analysis of the dynamic flow properties of chitosan in solution at different temperatures (25 - 45°C), chitosan concentration (0.5% - 2.0%), solvent type (acetic, lactic, and hydrochloric acid), and ionic strength (0 and 0.2M NaCl) has been undertaken. The storage modulus, G', loss modulus, G'' and complex viscosity, η^* have been determined over a wide range of frequencies and the results are presented using master curves. For the conditions studied, at low frequencies chitosan solutions show a constant complex viscosity which decreases as frequency increases. Likewise, storage modulus, G' and loss modulus, G'' increase as frequency increases with *G''* being always greater than *G'* ($\eta' > \eta''$) indicating that viscous effects are more important than elastic effects. For modelling the oscillatory-shear results we used the generalized Maxwell model. Two empirical equations were used to correlate the data: Cox-Merz rule for viscosity and Laun's rule for primary normal stress difference. Both relations were found to represent our data for the experimental conditions studied.

Zusammenfassung:
Eine ausführliche Analyse der dynamischen Fließeigenschaften von gelöstem Chitosan bei unterschiedlichen Temperaturen (25 - 45°C), unterschiedlichen Chitosankonzentrationen (0,5 - 2%), unterschiedlichen Lösungsmitteln (Essig-, Milch- oder Salzsäure) und unterschiedlicher Ionenstärke (0 und 0.2M NaCl) wurde durchgeführt. Der Speichermodul G', der Verlustmodul G'' und die komplexe Viskosität η^* wurden über einen weiten Frequenzbereich gemessen und die Resultate werden mit Masterkurven dargestellt. Innerhalb der studierten Bedingungen zeigen die Chitosanlösungen bei niedrigen Frequenzen eine konstante komplexe Viskosität, die sich jedoch mit steigender Frequenz verringert. Die Speicher- und Verlustmoduli erhöhen sich mit steigender Frequenz wobei G'' stets größer als G' ist ($\eta' > \eta''$). Dies deutet darauf hin, dass die viskösen Effekte einen größeren Einfluss als die elastischen Effekte einen größeren Einfluss als die elastischen Effekte haben. Zur Modellierung der Oszillationsmessungen wurde das verallgemeinerte Maxwellmodell benutzt. Zur Erstellung einer Korrelation zwischen den Daten wurden zwei empirische Gleichungen verwendet: die Cox-Merz-Regel für die Viskosität und die Laun-Regel für die erste Normalspannung. Beide Beziehungen waren geeignet, um unsere Daten für die gegebenen experimentellen Bedingungen darzustellen.

Résumé:
Une analyse détaillée des propriétés dynamiques en écoulement de solutions de chitosan à différentes températures (25 - 45°C), différentes concentrations de chitosan (0,5 - 2,0%), différents types d'acide (acétique, lactique, et chlorhydrique) dissolvant, et différentes concentrations ioniques (0 et 0.2M de NaCl) a été entreprise. Le module élastique, G', le module de perte, G', et la viscosité complexe, η^* ont été déterminés sur un éventail de fréquences et des résultats sont présentés en utilisant des courbes maîtresses. Pour les conditions étudiées, la viscosité complexe est constante à basses fréquences et diminue lorsque la fréquence augmente. De même, le module élastique, G', et le module de perte, G'', augmentent avec l'augmentation de la fréquence, G'' étant toujours supérieur à G' ($\eta' > \eta''$) indiquant que les effets visqueux sont plus importants que les effets élastiques. Pour modéliser les résultats en cisaillement oscillatoire, nous avons employé le modèle généralisé de Maxwell. Deux équations empiriques ont été employées pour corréler les données: la règle de Cox-Merz pour la viscosité et la règle de Laun pour la première différence des contraintes normales. Les deux relations se sont avérées valides pour représenter nos données dans les conditions expérimentales étudiées.

Key Words: Chitosan, Cox-Merz and Laun rules, dynamic rheology, Maxwell model

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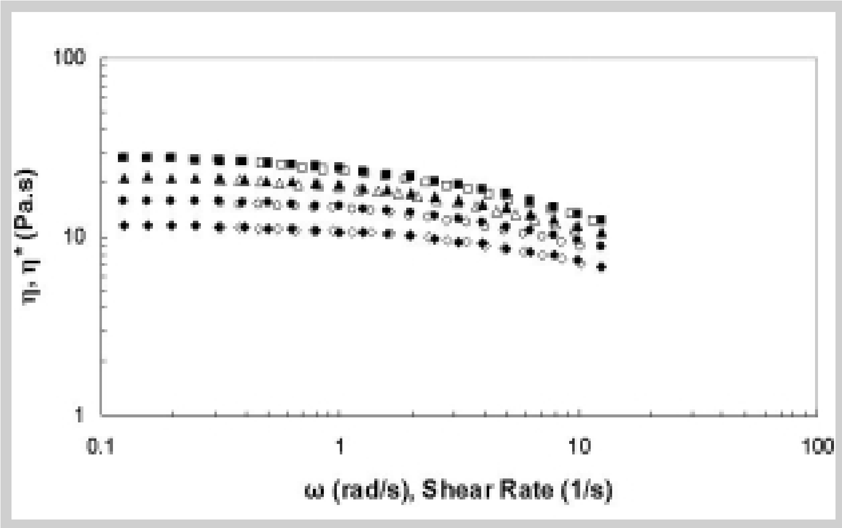

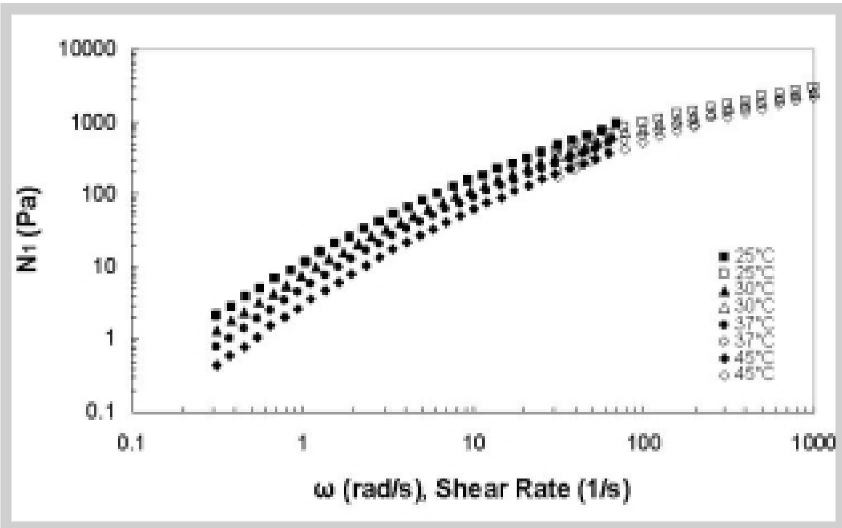

Figure 6 (above): Comparison of the Cox-Merz rule for a 2% chitosan solution in 1% acetic acid at different temperatures. Closed symbols are steady-shear viscosity, η, and open symbols are complex viscosity, η. Each symbol corresponds to a different temperature: ■□ 25°C, ▲△ 30°C, ●○ 37°C, ◆◇ 45°C.*

Figure 7 (below): Comparison of primary normal stress difference obtained using Laun's rule (closed symbols) and experimental data (open symbols) for 2% chitosan solutions in 1% acetic acid.

to the complex viscosity ,η^*, at low frequencies. These results validate the data obtained by both rheological methods: steady-shear and oscillatory-shear tests.

Finally, Laun's rule (Eq. 10) was used to determine primary normal stress differences, N_1. This rule was applied to all chitosan solutions studied and the results are in agreement within experimental error. Figure 7 shows the results for 2.0% chitosan in 1.0% acetic acid solution at different temperatures. While Laun's rule data begins only at shear rate as low as 0.3 s^{-1}, N_1 experimental data starts at 30 s^{-1}.

CONCLUSION

For the experimental conditions studied, chitosan solutions, as many high molecular weight biopolymer and polyelectrolytes, showed non-Newtonian shear-thinning behaviour with normal stresses. Oscillatory-shear tests have shown that the loss modulus, G'', is always higher than the storage modulus, G', indicating that viscous effects are more important than elastic effects in chitosan solutions (no crossover point in the experimental range studied). The generalized Maxwell model was found adequate to represent the fluid character of the solutions, in general six Maxwell-parameters are sufficient to fit the curves in the range studied.

At high chitosan concentrations the moduli are almost independent on the presence of salt. When the chitosan concentration decreases, differences between the moduli of the solutions with and without salt are observed. The presence of a counterion led to lower moduli values. However, this effect is suppressed when chitosan was dissolved in HCl, due to the excess number of chloride ions This indicates a suppression of electrostatic interactions that maintain the rheological properties almost constant.

A relationship between the effects of acid and the presence of counterions was shown, both factors influencing the electrostatic equilibrium in the solutions. The presence of a strong acid or the addition of NaCl induces strong interactions between chitosan and the medium. This is mainly related to the different neutralization and intramolecular electrostatic repulsion effects and to steric effects exerted by anions.

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