VISCOELASTIC PROPERTIES OF Na–ALGINATE SOLUTION

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The evolution of oscillatory–induced structure of Na–alginate solutions was studied for various frequencies and concentrations. The specific rate of elastic modulus increase, as well as the specific rate of loss modulus increase were used as a measure of chains flexibility in the flow field. The results were compared with the theory of Rouse proposed for flexible chains. All values of the specific rate of elastic modulus increase and the specific rate of loss modulus increase were higher then value from Rouse theory, indicating specific scaling and high rigidity of Na–alginate chains.

From both the fundamental and applied points of view, there is a growing interest in the characterization of the viscoelastic properties of alginate solutions (Serp et al., 2000; Simpson et al., 2003). Alginates have been used to encapsulate a variety of biological materials, including cells. Alginates are a family of unbranched polysaccharides with properties widely depending on their composition changes. However, the interpretation of the inter– and intra–molecular structure relations for polysaccharides from corresponding dynamical data is not an easy task.

The viscoelastic properties of Na–alginate chains are examined from oscillatory measurements. The elastic modulus (G') and loss modulus (G") represent the chain behavior in oscillating flow field. The elastic modulus depends on the inter–segment contact number and the mean energy stored per contact. The elastic modulus increases with frequency. The loss modulus depends on the energy dissipation due to conformational rearrangements of chain and chain–chain interactions. It also increases with frequency. For dilute Na–alginate solutions, the energy dissipation due to conformational rearrangements is expected, while the chain–chain interactions could be neglected. However, for concentrated solutions chain–chain interactions have dominant role on energy dissipation.

The Na–alginate rearrangement in flow field depends on flexibility of the chains. When specific, strong interactions such as hydrogen–bonding or electrostatic forces are present, chains conformations can suffer entropic frustration and behave as rigid polymer chains (Lodge, 1996). Several of these features are exposed in biological macromolecules. Hydrodynamics of rigid chains were analyzed in theories of Kirkwood and Auer (rods) and Cerf and Scheraga (ellipsoids) (Ferry, 1980). However, hydrodynamic of flexible chains were successful describes by theories of Rouse and Zimm (Lodge, 1996) wherein the chains were modeled as a series of N+1 segments connected by N Hookean springs, embedded in a continuum. In the theory of Rouse, hydrodynamic interactions between segments of chains were ignored, while the theory of Zimm included these conditions. The results of such theories can be interpreted in terms of scaling theory, an abstract but very general concept in polymer physics, developed by de Gennes (1979). Theories of Rouse and Zimm can be presented by scaling lows of both, the elastic modulus G' and loss modulus G", as $G' \approx \omega^{d'}$ and $G'' \approx \omega^{d''}$, where ω is frequency. Scaling exponents d', d" are equal to 0.5 for Rouse theory and 0.6 for Zimm theory.

In this study we investigate the effects of flexibility of Na–alginate chains on the linear viscoelastic properties, by using theory of scaling and comparisons with the theory of Rouse.

MATERIAL AND METHODS

Four concentrations of samples (produced from FMC BioPolymer, Norway) were prepared by dissolving powdered alginate in physiological solution (0.90% NaCl) and appropriate quantity of the distilled water was added. Solution rheology was studied in Rheometrics Mechanical Spectrometer RMS–605 using cup and pot device, at room temperature. Oscillating frequency was varied in the range 10^{-1} to 10^{2} Hz with 0.3 mrad amplitude.

RESULTS AND DISCUSSION

The elastic modulus as function of frequency and Na–alginate concentration is shown on Figure 1. The elastic modulus increases with frequency and with Na–alginate concentration. The frequency increase as well as the Na–alginate concentration increase, are expected to produce an increase of number of elastic contacts, between chains in solution.

The loss modulus as function of frequency and Na–alginate concentration is shown on Figure 2. The loss modulus increases with frequency and with Na–alginate concentration. The increases of frequency as well as the Na–alginate concentration, generate an increase of energy dissipation due to chain–chain interactions. The specific rate of elastic modulus increase (d') is shown in Figure 3 as function of Na–alginate concentration., together with the specific rate of increase of loss modulus (d").

All values of d' and d" are higher then value of 0.5 from the theory of Rouse. It is a consequence of

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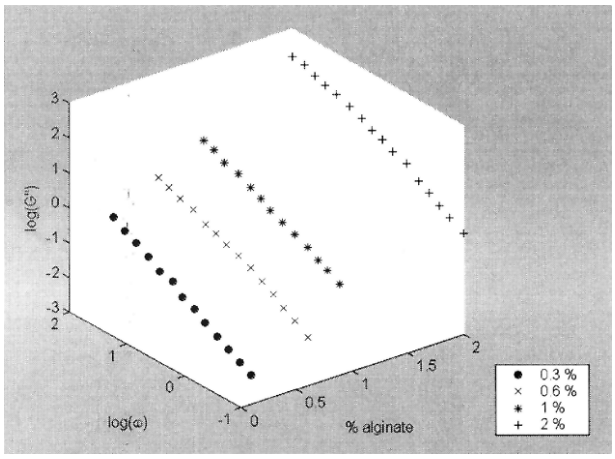

Figure 1. The elastic modulus vs. frequency and Na–alginate concentration.

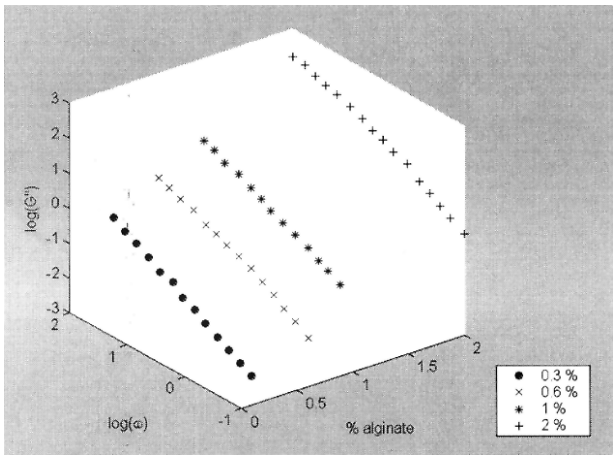

Figure 2. The loss modulus vs. frequency and Na–alginate concentration.

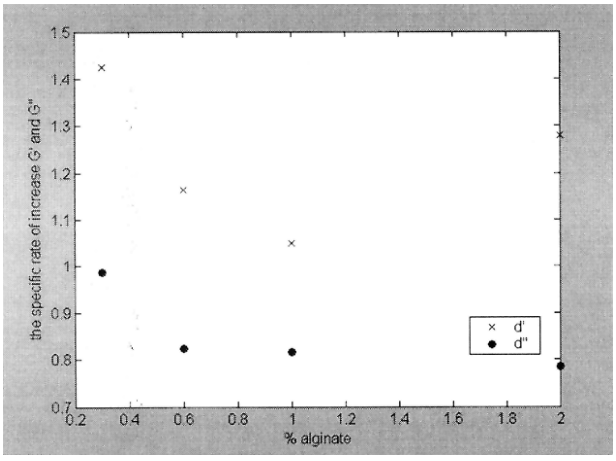

Figure 3. The specific rate of increase G' and G" vs. Na–alginate concentration.

Na–alginate chain rigidity. Flexible polymer chains form coils. For low frequencies, coil deformations occur. The short–range hydrodynamic interactions are dominant and determine the viscoelastic properties of the system. For further increase of frequency coil–to–rod transitions could be occurred. The long–range hydrodynamic interactions are dominant in such case. However, those rigid polymer chains behave as rod–like chains. When solution of rod–like chains is in to oscillatory flow field, chains orientation occur. The specific rate of rigid chains response to flow field action must be higher then the value of 0.5 (theory of Rouse) due to hydrodynamic interactions.

The specific rate of elastic modulus increase (d'), decreases with concentration till minimum at 1% Na–alginate concentration, $d'_{min} = 1.05$, with further increase. Decreases of d' could be explained as consequence of long–range hydrodynamic interactions between chains which increase with the inter–chain distances decrease. Long–range hydrodynamic interactions produce decrease of chain flexibility. For Na–alginate concentrations higher than 1% inter–chain distances decrease resulting in the increase of elastic contacts between chain segments and corresponding value of d'.

The specific rate of loss modulus increase (d") decreases with concentration. When the concentration of Na–alginate increases, inter–segment interactions increase, which cause increase the dissipation of energy as well as increase of loss modulus.

CONCLUSIONS

The Na–alginate solutions behave as ensemble of rigid chains due to strong hydrogen–bonding interactions. Chain flexibility is examined, considering scaling of modulus with frequency and its concentration dependence. The specific rate of the system response to oscillatory flow, i.e. scaling exponent expressed as scaling of elastic modulus and of loss modulus is higher then predicted from Rouse theory. It indicates high rigidity of alginate molecules because the value of 0.5 from theory of Rouse which is proposed for flexible chains. The scaling exponent of elastic modulus decreases with concentration, showing minimum at 1% Na–alginate concentration and further increase. The elastic modulus frequency scaling exponent decreases, due to flexibility of chain decrease. Further increase of d' could be understood as result of the increase of elastic contacts between chain segments. The specific rate of increase of loss modulus decreases with concentration due to inter–segment interactions increase.

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