

Capillary Microfluidics for Viscoelastic Characterization of Biopolymers

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Statement of Purpose: A very important rheological property of biopolymers is viscoelasticity and an effective way to assess the viscoelastic behavior of biopolymers is to measure their relaxation time. The global aim of the studies described here was to establish capillary microfluidics as a simple tool for analyzing the relaxation time of biopolymers. Viscoelastic studies of polymer solutions using capillary microfluidics have been reported in the literature [1, 2] but these studies do not explain the experimental results utilizing the molecular theory of viscoelasticity. The current study, similar to past studies, employed the Maxwell constitutive equation to determine the relaxation time of biopolymer solutions. However, this study explained and interpreted the experimental results using the Zimm-Rouse molecular theory of viscoelasticity.

Methods: Experiments were performed to reveal how the relaxation time of two different biopolymers, chitosan and DNA, was affected with a change in the length of the molecule (molecular weight) as well as with a change in concentration of their aqueous solutions. The different molecular weights of chitosan studied were 3 million, 1.5 million and 0.2 million and the molecular weights of DNA were 8.58 million, 1.32 million and 0.462 million. For each of these different molecular weights of chitosan and DNA, aqueous solutions of concentrations 0.01 μM , 0.02 μM , 0.05 μM and 0.1 μM were prepared. A droplet of the biopolymer solution was made to form at the tip of a glass capillary (Sutter Instruments, Novato, CA, USA) of inner diameter 1.10 mm, using a syringe-micrometer fluid delivery system. This droplet grew at the tip of the capillary until it came in contact with another capillary (inner diameter = 0.5 mm), which caused an instantaneous rise of the fluid. A video camera (HDR-SR5, Sony, Japan) was used to capture the rise of the fluid as it was transferred from one capillary to the other. The recorded movie was split into frames using the Windows Movie Maker software of Windows XP (Microsoft, WA, USA) and each video frame was analyzed by NIH Image Analyzing Software (National Institutes of Health, MD). All the experiments were performed at room temperature (22°C). Maxwell model for an Oldroyd fluid B was used to determine the relaxation time of biopolymer solutions from an analysis of their capillary rise (λ_e). This experimental relaxation time (λ_e) was compared to the relaxation time calculated using the Zimm-Rouse molecular theory (λ_m).

Results: For a given molecular weight of biopolymer, relaxation time increases with an increase in biopolymer concentration (Figure 1). Relaxation time also increases with molecular weight of the biopolymer for a given concentration. When the experimental relaxation time (λ_e) is compared to the relaxation time calculated from the

Zimm Rouse molecular theory (λ_m), it is seen that an adjustable parameter ϵ is required in the molecular theory in order to match λ_m and λ_e .

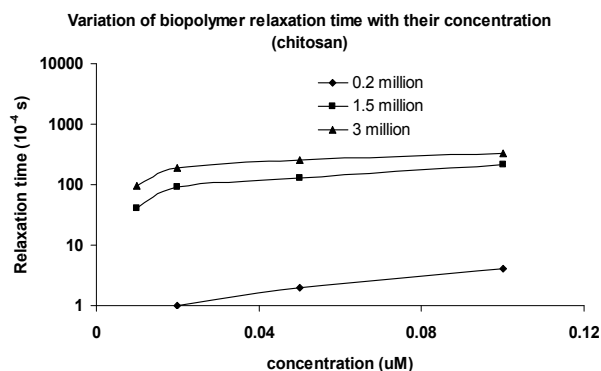


Figure1: Variation of relaxation time of different molecular weights of chitosan with concentration of their aqueous solutions.

Conclusions: The relaxation time of a polymer is the time required for its constituent chains to return to their equilibrium coiled state after the removal of a shearing force. For a given molecular weight of a biopolymer, when its concentration increases, the total number of polymer chains present in the solution increases. Consequently these chains face more resistance from one another on their way returning to the equilibrium state. Also, with an increase in concentration, the viscosity of the solutions correspondingly increases and the biopolymers face increasingly more resistance from their immediate fluid environment. At a given concentration of biopolymer solution, when the length of the constituent chains (molecular weight) increases, the increased length causes an increase in relaxation time. The parameter ϵ is used to match the experimental (λ_e) and molecular (λ_m) relaxation times. The study finds that the value of ϵ keeps increasing with an increase in biopolymer concentration as well as with an increase in molecular weight of the biopolymer. This indicates that the relaxation time calculated from the molecular theory (λ_m) overpredicts at lower concentrations and at lower molecular weights whereas it underpredicts at higher concentrations and higher molecular weights. This is consistent with a known limitation of the molecular theory that it neglects the effects of hydrodynamic interactions between the polymer molecule and the solvent. The adjustable parameter ϵ accounts for this hydrodynamic interaction and accordingly adjusts the end-to end distance of a polymer molecule at extension as a result of shearing force.

References: [1] Bazilevsky AV. J.Colloid Interface Sci. 2003; 262:16-24 [2] Kornev KG. J.Colloid Interface Sci. 2003; 262:253-62.