



Rheological studies of hyaluronan solutions based on the scaling law and constitutive models



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ABSTRACT

We have investigated the scaling relationship between rheological behavior and concentration for both salt-free and saline solutions of hyaluronan (HA), and adopted three viscoelastic constitutive models to predict the linear/non-linear viscoelastic behavior of these aqueous solutions of HA with different molecular weights at different concentrations up to 20 mg/ml. A series of concentration equations are obtained to describe the influence of HA concentration on solution viscosity. Corresponding to dilute and semi-dilute concentration region, salt-free HA solutions have scaling relationship between specific viscosity and HA concentration as $\eta_{sp} \sim c^{1.0}$ and $\eta_{sp} \sim c^{3.5}$, respectively, while for 0.15 M NaCl HA solutions, the scaling exponents are 1.5 and 4.2, respectively. Simulation results indicate that these constitutive models have good applicability to describe quantitatively the rheological properties of HA entangled solutions under either dynamic or steady shear flow. In addition, the plateau modulus scaling of HA solutions can be well described by the concentration-dependent length scale.

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1. Introduction

Hyaluronan (HA) is a linear, polyanionic, polysaccharide composed of (1→4)-β-D-glucuronic acid and (1→3)-β-D-N-acetyl glucosamine disaccharide repeating units [1]. HA has been supposed to be the only mucopolysaccharide found in nature, from bacteria to human beings. Besides its important physiological functions, the viscoelasticity of HA aqueous solution is of equal importance. In vivo HA has the function of maintaining moisture, adjusting osmotic pressure, maintaining organized form, barriering diffusion, lubricating joints and absorbing stress, all essentially related to its viscoelasticity [2]. The molecular weight (M_w) of HA can be in the order of several million, resulting in a very viscous aqueous solution with high viscoelasticity even at a low concentration. In an aqueous solution HA molecules adopt a worm like chain conformation [3,4]. The critical overlap concentration of HA with high M_w was reported to be about 1 mg/ml [5–7]. As one of the main components of synovial fluid in human body, the biological function of HA also includes the maintenance of viscoelasticity of liquid connective tissues, which is directly related to the lubrication and shock absorption by synovial fluid. It has been shown that the synovial fluid acts as a viscous liquid in the low-

frequency region (corresponding to a slow joint movement), but presents elastic behavior in the high-frequency region (corresponding to a rapid joint movement) [8]. Therefore, the rheological properties of HA have been emphasized by many researchers in papers [3,7,9–19], these studies are also important references for the commercial development and application of HA [19] as a product. At present, many medical applications, such as viscosupplementation for treating osteoarthritis, rheumatoid and traumatic arthritis; viscosurgery for cataract, glaucoma trabeculectomy and corneal transplantation; viscoaugmentation for replacing intercellular substance and lacked soft tissue; all involve closely the unique viscoelasticity of HA [5,9–12]. In addition to the medical field, HA has been also widely used in the pharmaceutical and cosmetic industries [20,21].

Most of the previous work focused on the viscosity property of HA saline solution partially based on the consideration and requirements of medicine application [9–15]. Theoretically, the rheological behavior of a polyelectrolyte in salt-free solution is different from that in saline solution, which can be readily observed in the dilute solution region where the relationship between concentration and viscosity becomes complex [22]. As a type anionic polyelectrolyte, HA has different rheological properties in salt-free and saline solutions. For example, Nishinari et al. [18] pointed out that the solution modulus of HA decreased during frequency sweep as the concentration of NaCl was more than 0.05 M due to the screening effect of electrostatic repulsion between anionic groups

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in HA chains surrounded by cations. Nevertheless, although the addition of salt to polysaccharide solution generally leads to the collapse of the molecular chain thus decreasing the solution viscosity, the salt added can also promote the interactions between macromolecules thereby giving rise to an apparent increase in the viscosity as seen in xanthan solution [22].

Polysaccharide solutions are usually typical complex fluids. This is mainly attributed to the complexity in the special chain structure, the variability in conformation of polysaccharide, and the constant occurrence of inter- and/or intra-association/interaction in solution. The flexibility of molecular chains, the M_w and molecular weight distribution, and the type and location of the substituent groups etc. also strongly influence the viscoelasticity of polysaccharide solutions. Furthermore, taking into account the influence of the polymer concentration, there is a wide range of variation in the viscoelasticity of polysaccharide in dilute to concentrated solutions. In addition, many polysaccharides are polyelectrolytes whose viscoelasticity is significantly influenced by various ions. It is hard thus to establish an elaborately physical model that correlates molecular parameters of the polysaccharide to theoretically simulate and predict the viscoelasticity of the polysaccharide. For polysaccharide solutions with entangled semi-flexible chains, their rheological behavior conforms to the Cox–Merz rule. Generally, these solutions obey the viscous fluid models such as the Cross model [23] and Carreau model [24]. Although these models can describe the shear rate dependence of the steady-state viscosity for viscous fluids, for complex viscoelastic fluids, more complex non-linear viscoelastic models may have a comparative advantage in predicting their steady-state viscoelastic behavior. As for their dynamic viscoelastic behavior, it can also be described by some complex viscoelastic models. Theoretically, due to the aforementioned complicated properties, modeling work for the polysaccharide solutions is still a challenge, even though a lot of work related to synthetic polymer solutions and melts has been done. There are numerous studies regarding the rheological properties of polysaccharide solutions, however, the studies on theoretical simulation and model calculation of the viscoelastic behavior of polysaccharide solutions are rarely reported, especially in the aspect of successful using some non-linear viscoelastic models [25].

The aim of the present work is to scale the viscosity behavior and to provide a method for quantitative calculation and prediction of the viscoelasticity of HA solutions. A multi-mode linear Maxwell viscoelastic model and two kinds of network theories based non-linear viscoelastic constitutive models, Phan-Thien Tanner (PTT) [26] and Giesekus [27], were employed to simulate numerically the dynamic and steady shear data. Details of the rheological behavior in entangled HA solutions were focused.

2. Experimental

2.1. Materials

The HA samples with different molecular weights (HA-1, HA-2 and HA-3) were obtained from Shandong Freda Biopharm Co., Ltd. (China). A detailed molecular characterization based our previous work [28] was carried out using size exclusion chromatography–light scattering (Viscotek TDA 305, Malvern Instruments, USA), or size exclusion chromatography connected in series to a UV detector (SPD-6A, Shimadzu, Japan), a MALLS detector (Dawn[®] DSP, Wyatt Technology Corporation, USA), and a Refractometer (RI 2000, Schambeck SFD GmbH, Germany). The results showed that the weight average M_w , polydispersity index and z-average radius of gyration (R_g) were 1.27×10^6 , 1.56, 108.8 nm for HA-1; 1.80×10^6 , 1.27, 178.3 nm for HA-2; and 2.88×10^6 , 1.06, 189.2 nm for HA-3, respectively.

2.2. Preparation of HA solutions

An appropriate amount of HA was dispersed in distilled water and left tumbling on a roller–mixer till hydration was complete.

2.3. Rheological measurements

The dynamic and steady-state shear measurements were carried out using a rotational rheometer AR G2 (TA Instruments, USA) with a 2°1'8" cone plate geometry (60 mm in diameter). The temperature was regulated by a circulating water bath and Peltier system at 25 °C. The shear rate in steady-state measurements was ranged from 0.01 to 1000 s⁻¹. The angular frequency in small amplitude oscillatory shear (SAOS) measurements was ranged from 0.01 to 100 rad/s. The dynamic measurements were performed within the linear viscoelastic region. To avoid the evaporation of water from the sample during the measurement, a thin layer of low-viscosity silicone oil was placed on the periphery of the surface of the sample held between the plates.

2.4. Theoretical calculations

In the limit of small deformations, polymeric fluids show a linear viscoelastic response and can be accurately described by a multi-mode Maxwell model. In this work, a differential form of the upper-convected Maxwell model was used [29]:

$$\overset{\nabla}{\tau}_i + \frac{1}{\lambda_i} \tau_i = 2G_{ei}D \quad (1)$$

where τ is the extra stress tensor, $D = 1/2(L + L^T)$ is the rate of deformation tensor, in which L is the velocity gradient tensor and T denotes the transpose of a tensor. λ_i is the i th linear relaxation time and G_{ei} is the plateau modulus of the i th mode. The upper-convected time derivative of the stress $\overset{\nabla}{\tau}_i$ is defined as [30]:

$$\overset{\nabla}{\tau}_i = \dot{\tau}_i - L \cdot \tau_i - \tau_i \cdot L^T = \frac{\partial \tau_i}{\partial t} + \vec{u} \cdot \vec{\nabla} \tau_i - L \cdot \tau_i - \tau_i \cdot L^T \quad (2)$$

To describe the non-linear rheological behavior of the semi-flexible macromolecular chains in HA solutions, two non-linear viscoelastic models of the differential type, Phan-Thien Tanner (PTT) [26] and Giesekus [27], were employed.

For the upper-convected time derivative PTT model, a simplified multi-mode PTT model was written as [30]:

$$\overset{\nabla}{\tau}_i + \frac{1}{\lambda_i} \left[e^{(\varepsilon_i/G_i)\text{tr}(\tau_i)} I \right] \cdot \tau_i = 2G_{ei}D \quad (3)$$

For the upper-convected time derivative Giesekus model, a multi-mode Giesekus model can be simplified to [31]:

$$\overset{\nabla}{\tau}_i + \frac{1}{\lambda_i} \left[\frac{\alpha_i}{G_i} \tau_i + I \right] \cdot \tau_i = 2G_{ei}D \quad (4)$$

where α_i is nonlinear factor.

3. Results and discussion

3.1. Steady-state shear of HA solution in non-linear viscoelastic region

Shear-thinning is a well-known property of polymer solutions with typical of entangled network. The rheological response of the network is controlled by the entanglement formation and disruption rates. Under low shear the two rates are equal whereas with

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