



Particle tracking microrheology of the power-law viscoelasticity of xanthan solutions



Aristeidis Papagiannopoulos*, Konstantinos Sotiropoulos, Stergios Pispas

Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48 Vassileos Constantinou Avenue, 11635, Athens, Greece

ARTICLE INFO

Article history:

Received 4 February 2016

Received in revised form

16 May 2016

Accepted 17 May 2016

Available online 18 May 2016

Keywords:

Particle tracking

Microrheology

Xanthan

Polysaccharide

Viscoelasticity

Renaturation

ABSTRACT

We use particle tracking microrheology to obtain the power-law dynamical behaviour of xanthan in several aqueous solution conditions and illustrate that the probe particle motion is subdiffusive even at low xanthan concentrations. Analysis of the concentration dependence of xanthan's viscoelasticity is described in terms of linear and comb polyelectrolyte rheological models. There is a clear distinction between two power-law regimes i.e. unentangled and entangled of the modulus prefactor as a function of concentration. The critical entanglement concentration and the power-law exponents are investigated in terms of their dependence on the content and valency of the added salts. Above the entanglement concentration the deviation of the particles motion from Brownian diffusion depends strongly on concentration. Linear complex viscosity is compared to nonlinear steady shear rate viscosity in an illustration of predicting the nonlinear rheology from particle tracking measurements in food biopolymer solutions. Finally in renatured xanthan solutions the viscoelasticity enhancement by temperature treatment is demonstrated to be more effective in the entangled region.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Xanthan gum is a high molecular weight anionic polysaccharide secreted by the microorganism *Xanthomonas campestris* and is produced commercially by a fermentation process (Sworn, 2009). It consists of a cellulosic backbone with short side-chains emerging every other glucose (Born, Langendorff, & Boulenguer, 2005; Sworn, 2009). The trisaccharide side chains contain a middle glucuronic acid group between two mannose units. The terminal mannose group may carry pyruvate residues and the internal one may be acetylated in various degrees depending on the fermentation process (Sworn, 2009; Wyatt & Liberatore, 2010). Xanthan has seen wide research interest during the 3–4 decades because of its excellent rheological behaviour and approval as food additive which can be used with no specific restriction (Born et al., 2005). Other than its role in food industry as a viscosity modifier, it finds use in pharmaceutical controlled release applications and as an oil recovery agent in oil industry (Katzbauer, 1998; Xu, Xu, Liu, Chen, & Gong, 2013). In particular chitosan–xanthan polyelectrolyte complexes have shown potential in gastrointestinal drug delivery

systems with pH responsive swelling properties (Luo & Wang, 2014). Additionally it interacts synergistically with guar gum for viscosity increase and with locust bean gum for gelation (Katzbauer, 1998; Sworn, 2009). Xanthan's physiological function has also been pointed out because it is the predominant component in the biofilms of *Xanthomonas campestris* where, in analogy to other exopolysaccharides, it prolongs bacterial cell survival and increases their resistance to temperature and UV light (Born et al., 2005).

In solutions of adequate salt content xanthan molecules are in a broken helix conformation, where the helical conformation of the backbone is stabilized by hydrogen bonding and the absence of strong electrostatic repulsions between the charged side-chains (Muller, Aurhourrache, Lecourtier, & Chauveteau, 1986; Rochefort & Middleman, 1987). The helical structure melts during a broad transition around 50–60 °C because of the destabilization and denaturation of the helical secondary structure. This is the widely studied order–disorder or helix–coil transition of xanthan (Choppe, Puaud, Nicolai, & Benyahia, 2010; Milas, Reed, & Printz, 1996; Norton, Goodall, Frangou, Morris, & Rees, 1984; Pelletier, Viebke, Meadows, & Williams, 2001). Light scattering experiments revealed that increasing the temperature of xanthan solutions at 0.1 M NaCl resulted to a reduction in the apparent molecular weight pointing to a possible disruption of double-stranded intermolecular

* Corresponding author.

E-mail address: apapagiannopoulos@eie.gr (A. Papagiannopoulos).

helices with no evidence of re-association in the renatured samples (Capron, Brigand, & Muller, 1997). Sato et al. (Matsuda, Biyajima, & Sato, 2009) and Matsuda et al. (Matsuda, Sugiura, Mays, & Tasaka, 2015) illustrated that native xanthan in dilute solutions exists in double-helix dimers that dissociate in unimers above 80 °C and form double helical hairpin loops in the renatured state. At higher concentrations portions of double helices are not reconstructed within an individual dimer but form higher aggregates of inter-connected dimers during renaturation.

In semi-dilute aqueous solutions xanthan forms weak gels (Cuvelier & Launay, 1986) with power-law behaviour (Jaishankar & McKinley, 2014) that originates from its self-similar organization in multiple length scales. The absence of a terminal relaxation time for a wide temporal regime can be attributed to its extended conformation and its ability to form intermolecular bridges (Wyatt & Liberatore, 2010). Hydrogels commonly need at least two characteristic length scales for their spatial description, one corresponding to the correlation length (average distance between chain segments) and one to the characteristic distance of the large length scale inhomogeneities (Shibayama, 2011) that define spatial limits in fractal morphology.

Passive microrheology methods (Cicuta & Donald, 2007; Papagiannopoulos, 2016; Waigh, 2005) are based on the thermal motion of particles within fluids, the measured response is linear by-definition and they have spatial sensitivity in the nanoscale. This way microrheology is ideally suited for studying fragile soft materials as linear and comb synthetic (Di Cola, Waigh, & Colby, 2007; Papagiannopoulos, Fernyhough, & Waigh, 2005) and biological polyelectrolytes (Georgiades, Pudney, Thornton, & Waigh, 2014; Papagiannopoulos, Waigh, Hardingham, & Heinrich, 2006; Yakubov, Papagiannopoulos, Rat, Easton, & Waigh, 2007), gelling systems (Corrigan & Donald, 2009; Larsen, Schultz, & Furst, 2008) and semirigid filamentous proteins (Tassieri, Evans, Barbu-Tudoran, Khaname, Trinick, & Waigh, 2008). In this article we apply video particle tracking microrheology (VPTMR) to directly probe the power-law dynamic nature of xanthan solutions at intermediate frequencies (0.3–25 rad/s) and relate the rheological picture with the well documented viscoelastic properties of linear and comb polyelectrolytes. Additionally we report on the expected spatial fractal exponents of the xanthan fluids under the assumption of screened excluded volume interactions. Finally the linear response extracted by video particle tracking is compared against the shear thinning power-law viscosity obtained by nonlinear steady shear flow measurements in an illustration of using particle tracking microrheology for estimating industry relevant properties for polysaccharides.

2. Materials and methods

2.1. Materials and sample preparation

Xanthan gum was purchased from CP Kelco and was used without further treatment. It has a high molecular weight (Pelletier et al., 2001), (Wyatt & Liberatore, 2010) of about $2 \cdot 10^6$ g/mol with a broad distribution (PDI~2). The powder was dissolved in distilled water under stirring and stored overnight at 4° C. Salt content was adjusted by adding small amounts of concentrated salt solutions (NaCl or CaCl₂) up to the desired volume and the samples were again stored at 4° C overnight. For video particle tracking microrheology experiments polystyrene (PS) microspheres 0.528 μm in diameter were purchased from Polysciences. Their concentration in final solutions was about $5 \cdot 10^{-4}$ v/v so that 40–50 particles were tracked simultaneously. The desired amount of microparticle dispersion was added to the solutions under stirring about 1 h before the particle tracking experiments. For renaturation protocols

1 ml of 0.1 M NaCl solution at the desired concentration was placed in an oven (inside a sealed glass vial) at preset temperature (60 or 80 °C) for 2 h. The sample was then cooled by placing the vial in a water/ice bath (Capron et al., 1997). All experiments were performed at room temperature.

2.2. Video particle tracking microrheology (VPTMR)

The thermal motion of PS probe microspheres was monitored by a bright-field Olympus BH2 microscope equipped with a 100× oil immersion lens. A Hitachi KP-M1A CCD camera was used to capture videos at 25 frames/s and a shutter exposure time at 0.02 s. The sample was loaded inside the cavity of a glass slide and covered by a thin glass cover slip. The lens was focussed approximately 15 μm underneath the cover slip so that any wall effects were negligible. The trajectories of the particles were extracted by IDL tracking software based on standard image analysis algorithms. The tracks of the fluctuating particles ($r(t)$) are utilized to extract the mean-squared-displacement (MSD) over their ensemble (N) and initial times (t) as a function of lag-time (Equation (1)).

$$\langle \Delta r^2(\tau) \rangle = \langle [r_N(t + \tau) - r_N(t)]^2 \rangle_{t,N} \quad (1)$$

A detailed account on the particle tracking procedure and analysis of particle trajectories can be found elsewhere (Crocker & Grier, 1996; Papagiannopoulos, 2016).

2.3. Viscosity measurements

Bulk viscosity measurements were performed on a Brookfield DV-1 PRIME cone-and-plate digital viscometer. The samples were introduced in the viscometer by placing the desired amount on the flat plate. The cone was gently lowered during contact. For a certain shear rate a viscosity measurement was taken after the torque equilibrated at a stable value. The experiment was run from low to high shear rates and reproducibility was checked by testing several shear rates (low and high) repeatedly. There was no sign of permanent transformation of the fluid. The limitations of the instrument in minimum and maximum measurable torque resulted to the presented range of measurable shear rates.

3. Results and discussion

The MSDs obtained by particle tracking from a series of xanthan aqueous solutions with no added salt and with 0.5 M NaCl are shown in Fig. 1. The MSD drops as the concentration increases which is a clear sign of increasing resistance of the fluid against particle motion. VPTMR is limited by the spatial resolution of the tracking system (microscope optics and tracking software) which in our apparatus is about 20–30 nm. This imposes a lowest boundary of the smallest detectable displacement and results to a static error (Papagiannopoulos, Waigh, & Hardingham, 2008; Savin & Doyle, 2005) which practically acts as a noise base-line for the measured MSD. Static error effectively sets the maximum viscosity (or modulus) and hence solution concentration that can be studied. Still the concentration range probed in this study is of industrial relevance as for example it overlaps with typical usage levels in food products (Sworn, 2009).

The MSD data sets appear linear (log-log representation) in the time-regime observed by the experiment hence power-laws (Equation (2)) are used to model their lag-time dependence (using A and a as fitting parameters).

$$\langle \Delta r^2(\tau) \rangle = A \cdot \tau^a \quad (2)$$

Download English Version:

<https://daneshyari.com/en/article/6987159>

Download Persian Version:

<https://daneshyari.com/article/6987159>

[Daneshyari.com](https://daneshyari.com)