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Visualization of micro-scale inhomogeneities in acrylic thickener solutions: A multiple particle tracking study

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ABSTRACT

Multiple Particle Tracking (MPT) microrheology in combination with bulk mechanical rheometry has been used to characterize the structural and viscoelastic microheterogeneity of commercial acrylic thickeners Carbopol EDT2050, Viscalex HV30, and Sterocoll D in aqueous solutions at technically relevant polymer concentrations. According to bulk rheology Carbopol solutions exhibit a much higher elasticity than Sterocoll and Viscalex solutions at low polymer concentration whereas all thickeners are composed of similar main monomers. MPT experiments confirm that the latter two systems form homogeneous predominately elastic polymer networks with a mesh size <200 nm. In contrast, Carbopol solutions are highly heterogeneous and the degree of heterogeneity strongly increases with increasing polymer concentration. Predominantly elastic and viscous regions within the solution can be identified based on the slope of the mean squared displacement of individual particle trajectories. This heterogeneity is directly imaged here for the first time using Voronoi diagrams and characteristic length scales varying from 5 to 20 μm are found. Additionally, variation of the probe size reveals that the elastic regions themselves are heterogeneous including areas with mesh size <200 nm and a larger fraction with mesh size between 200 nm and 500 nm.

1. Introduction

Synthetic acrylic polymers are frequently used as thickening agents in water-based coatings and adhesives or personal care products. Typically, these commercial alkali-swellable acrylates [1–4] (as well as various other polymeric thickeners) form inhomogeneous partly aggregated or cross-linked solutions. Inter- and/or intramolecular aggregation is due to hydrophobic groups randomly distributed along the chains and the swelling behavior can be varied via solvent quality [5–7]. Crosslinking can be induced either thermally or by adding appropriate crosslinking agents during synthesis. Accordingly, such thickener solutions cover a wide range of rheological behavior, ranging from weakly elastic, almost Newtonian to highly elastic gel-like. Despite its high technical relevance, little is known so far about the contribution of the micro-scale inhomogeneity to the bulk viscoelastic properties [8]. Here we use the method of Multiple Particle Tracking (MPT) to quantify the degree of structural and mechanical microheterogeneity of such acrylic thickener solutions. This technique was originally described by Apgar et al. [9] and Ma et al. [10]. Up to now MPT has been frequently used to study microheterogeneities of actin filament network [11–14], living cells [15–19], proteins [20,21], DNA solutions [22], biological gels [23,24] or yield stress fluids [1–3]. The fluid mechanics of microrheology has been described thoroughly [25,26]. The basic idea is to monitor the Brownian motion of inert fluorescent tracer particles by means of digital video microscopy. For homogeneous fluids the bulk shear moduli [27] can be determined using this technique, but more importantly the statistical analysis of tracer trajectories allows for a characterization of sample inhomogeneity. Al least some hundred particles have to be monitored simultaneously to allow for a significant statistical analysis in order to cover a sufficiently large area of the samples. For a better interpretation and characterization of the heterogeneous dynamics and/or microstructure, statistical distributions of displacement and local viscosity [11,22,23,28,29] but also van Hove correlation plots and the non-Gaussian parameter α [30–33] are used to characterize the heterogeneous and microstructure of fluids. The non-Gaussian part of the van Hove correlation function $G_s(x,\tau)$ [32,33] is defined as the probability density distribution of the displacements of individual particles [32,34]:

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$$G_s(x,\tau) = \frac{1}{N}\langle \sum_{i=1}^{N} \delta[x + x_i(0) - x_i(\tau)]\rangle = \frac{N(x,\tau)}{N} \quad (1)$$

with X the distance of particle center of mass along the X -coordinate. N(X,τ) is the number of particles found at positions between X and (X + d X) after lag time τ and N is the total number of particles. If all particles are exposed to similar environment $G_s(x,\tau)$ has a Gaussian form. Deviations from this form reflect the presence of heterogeneities. Such deviations can be characterized by the non-Gaussian parameter

$$\alpha = \frac{\langle x^4(\tau)\rangle}{3x^2(\tau)^2} - 1 \quad (2)$$

with $\langle x^b(\tau)\rangle = \sum_{i=1}^{N} x_i^b(\tau) * G_s(x,\tau)$ the simplest combination of the second (b = 2) and fourth (b = 4) moments of a one-dimensional probability density function. α is zero for a Gaussian distribution, while distributions result in large values of α [30,33].

In the first part of the paper, we characterize bulk rheological properties of the three different acrylic thickeners and investigate variations of yield stress σ_y and plateau modulus G_0 as a function of polymer concentration. In the second part, we describe and use the MPT method to perform microrheological measurements on thickener solutions presenting similar bulk elastic properties, i.e. similar G_0 values. For those samples, we generate the variation of mean square displacements (MSD) as a function of time and from statistical analysis of the MSD distribution we extract microstructural and micro-mechanical heterogeneity informations. Additionally, for Carbopol only we investigate probe size and polymer concentration effects on microrheological properties in order to get additional microstructural information. Finally, we use Voronoi diagrams constructed using the particle positions as generators in order to visualize the size and spatial distribution of heterogeneities based on a "rheological contrast", i.e. classification of particle mobility and hence viscoelasticity of its surrounding according to the slope of the respective MSD.

2. Materials and methods

2.1. Samples

Our experiments were performed using three acrylic thickeners, Sterocoll D, Viscalex HV 30 (both from BASF SE Ludwigshafen, Germany) and Carbopol ETD 2050 (Lubrizol Advanced Materials, Cleveland, USA). For brevity, we use the family name of each product in the subsequent text. These are commercial, alkali-swellable thickeners based on homopolymers and co-polymers of polyacrylic acid and a small amount of a crosslinking agent [7,35]. Upon neutralization the weak acrylic acid groups dissociate in aqueous environment, the polymer chains get soluble and the thickening properties are developed. Sterocoll is mainly used as rheology modifier for rotogravure and paper coating [36] and Viscalex for water-borne coating [37,38]. Both are synthesized in an emulsion polymerization process and delivered as a milky liquid with a solids content of 25%–30% and pH ≈ 2.5–3. In both cases, main monomers are ethylacrylate (EA) and methacrylic acid (MAA). Sterocoll is an alkali swellable emulsion polymer (ASE) with a MAA/EA molar ratio of about 50:50 and a small fraction of diethylenically unsaturated monomer as chemical crosslinker. Viscalex differs in a sense that it is a hydrophobically modified alkali swellable emulsion (HASE). It contains hydrophobic alkyl groups attached to its polymer backbone. The molar ratio MAA/EA/Alkyl is about 49:50:1. In aqueous solution, hydrophobic association junctions are formed providing side chains physical crosslinking. Structure representations for these types of polymers are shown in studies of Ng et al. [6], Dai et al. [39] and Wang et al. [5]. For the investigations presented here, aqueous solutions of Sterocoll with concentrations of 0.25–5wt. % and Viscalex with concentrations of 0.25–1.5 wt.% were prepared. Solutions were stirred at room temperature for 48 h and adjusted to pH = 8 by slowly adding 1 N NaOH [4,7]. Carbopol ETD 2050 consists of high molecular weight polymers, made up of homopolymers of acrylic acid and copolymers of acrylic acid and long chain (C10–C30) alkyl acrylate crosslinked with a polyalkenyl polyether. Illustration of the Carbopol structure is shown in Ref. [40]. The carboxylic groups are the principle chemical sites that affect the thickening characteristics. It is supplied as powder. We prepared samples (0.1–1wt.%) by slowly adding powder in water, which decreases the pH to 3 while stirring, consequently carboxylic groups release the hydrogen atom. The mixture was further stirred at room temperature for 48 h and adjusted to pH = 6 by slowly adding 4 N NaOH. Neutralization replaces a free hydrogen cation with the sodium cation and the repulsive force between the negatives charges of the carboxyl groups and osmotic pressure from mobile ions cause the structure to swell, resulting in a highly elastic microgel system optically transparent, but known to exhibit an inhomogeneous structure on the micrometer scale [1,2]. Increasing the pH further does not change the viscoelastic elastic properties very much. Carbopol is used in applications including clear gels, hydroalcoholic gels and lotions [41].

2.2. Mechanical measurements

A rotational rheometer Thermo MARS II equipped with a cone-plate measuring cell (diameter $d_{CP} = 60$ mm, cone angle $\alpha_{cone} = 1°$) was used to perform steady as well as small amplitude oscillatory shear experiments. The latter covering the frequency range from 0.01 to 100 rad.s^{-1}. Strain sweep experiments performed prior to frequency sweeps ensure that the strain amplitude used was sufficiently small to provide a linear material response at all investigated frequencies. The yield stress was determined by fitting a Herschel–Bulkley model to the shear rate/shear stress data obtained from stress ramp experiments covering the stress interval from 0.1 Pa to 50 Pa within a measuring time of 1800 s. All measurements were performed at 20 °C and a solvent trap was used to avoid evaporation of the solvent during the experiments.

2.3. Multiple-particle tracking (MPT) setup

MPT experiments were performed using an inverted fluorescence microscope (Axio Observer D1, Zeiss), equipped with a Fluar 100×, N.A. 1.3, oil-immersion lens combined with a 1x optovar magnification changer. We have tracked the Brownian motion of green fluorescent polystyrene microspheres of 0.19, 0.51 μm diameter (Bangs Laboratories: USA, lot Nr FC03F/7049) used as tracer particles. The mixture (total volume: ~20 μl) containing the sample solution including the tracers (volume fraction around 1%) was injected into a commercial rectangle capillary (CM Scientific Ltd, United Kingdom). The sample thickness was ~150 μm and the microscope was focused roughly halfway into the sample to minimize wall effects. Images of the fluorescent beads were recorded onto a personal computer via a sCMOS camera Zyla X (Andor Technology: 21.8 mm diagonal sCMOS Sensor size, 2560 × 2160 square pixels (6.5 μm), up to 50 frames/s in global shutter mode). Displacements of particle centers were monitored in an 84 × 84 μm field of view, for at least 100 s at a rate of 30 frames/s. For each experiment a total of roughly 300 particles were tracked simultaneously. Movies of the fluctuating microspheres were analyzed by a custom MPT routine incorporated into the software Image Processing System (Visiometrics iPS) and a self-written Matlab program [42]. Tracing errors due to particles moving in and out of the