Nanorheological analysis of xanthan/water solutions using magnetic nanoparticles with different particle sizes

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ABSTRACT

We studied have nanorheological properties (viscosity and shear moduli) of aqueous xanthan solutions, in the oscillation frequency range up to 10 kHz by using magnetic particles that undergo Brownian relaxation and frequency dependent AC susceptibility (ACS). We used two magnetic nanoparticle (MNP) systems with different mean particle sizes of 80 nm and 100 nm. The determined viscosity and shear modulus of the diluted xanthan solutions from the ACS measurement of the two particle systems agree with traditional oscillatory rheological measurements. However, there is a particle size dependency that could be explained by comparing particles sizes with the xanthan microstructure.

INTRODUCTION

The chewing and swallowing process of food is a combination of voluntary and involuntary actions, and it involves complex flow geometry as well as a mixture of shear and extensional flow during which aroma and taste are perceived. To study textural changes as expressed by the viscoelastic properties of the food directly in the mouth we investigate possibility the of using magnetic nanoparticles (MNP) as nanosized sensing probes. The use of MNP systems that undergo Brownian relaxation (stochastic particle rotation) enables us to remotely sense local viscoelastic properties. These properties can be estimated by measuring and analysing the frequency dependent AC susceptibility (ACS) of the MNPs when they are mixed with the substance that shall be analysed. The goal of using MNPs is to follow rheological properties, texture and aggregation remotely instead of using sensors with cables in the mouth as it is done today [1].

Iron oxide based MNPs are used in several biomedical applications such as in diagnosis, actuation, imaging and therapy [2,3]. MNPs and ACS analyses have been previously used in nanorheological studies in various concentrations of polyethylene glycol (PEG), gelatine and polymer melts [4, 5]. We have also reported on nanorheological studies of different xanthan/water solutions using MNPs with a median particle size of 80 nm [6]. Comparing the nanorheological studies with macroscopic oscillatory rheological measurements, we found that there is a good agreement between the two measurement techniques.

Xanthan gum is a microbial polysaccharide where the xanthan molecules consist of a branched primary structure with a (1-4)-linked- β -D glucose backbone with ionic side chains, which in solution behave as stiff, rod-like helices. The 3D structure of xanthan gum has voids between the molecular chains with sizes in the range of 100 nm (almost the same size as the used magnetic particle sizes), see Fig. 1 and ref. [7,8]. Xanthan solutions show a pseudoplastic flow behaviour with a yield stress, at very low xanthan concentrations, due to the stiffness and the charge of xanthan molecules [9,10]. Xanthan molecules in solution can form intermolecular connexions via hydrogen bonding and physical entanglements. At concentrations at which the hindrance between the repelling rods becomes larger, the rods 'freeze' in random orientation [10].

In this study we continue the nanodifferent rheological analysis on xanthan/water solution concentrations by using ACS. Different MNP sizes (using iron oxide based multi-core particles with mean particle sizes of 80 nm and 100 nm) are used to investigate the particle size effect on the viscoelastic properties of the solutions. In order to use magnetic nanoparticles in rheological studies the MNPs must relax via the Brownian relaxation (i.e. particle magnetic moment locked in a specific direction of the MNP), [11-14]. In a surrounding media that can be described only by a viscosity (for instance MNPs dispersed in water) the Brownian relaxation time, τ_B , can be described by.

$$\tau_B = \frac{3V_H \eta}{kT} \tag{1}$$

where V_H is the hydrodynamic volume of the MNP, η the viscosity, k the Boltzmann constant and T is the temperature.

ACS measurements have shown that both the 80 nm and 100 nm MNP systems used in this study exhibit Brownian relaxation with respect to the measurement time windows [11,13,14]. These MNPs are therefore sensitive to the surrounding viscoelastic properties [11,13].

MATERIALS AND METHODS

The MNP systems used in this study consist of commercially available iron oxide based multi-core particles BNF-Dextran with mean particle diameters of 80 nm and 100 nm (micromod Partikeltechnologie GmbH) with dextran as particle matrix material. The individual magnetic cores in the multi-core particles are in the range of 10 nm - 20 nm.

Electron Transmission Microscopy (TEM) images on MNPs mixed with xanthan can be seen in Fig. 1. Small droplets of the samples were quenched on gold cups in liquid propane, then transferred into the precooled freeze-fracture unit (Balzers BAF 400T). The samples were then placed in vacuum and the temperature was decreased to -100 °C. When the temperature was stabilized the samples were fractured and etched prior to the evaporation of platinum and carbon under rotation. The etching was about 100 nm in depth depending on the distance to the cold plate. The samples were then cleaned and collected on grids. The freeze fractured samples were analysed in a transmission electron microscope (TEM), LEO 906E.

For the ACS analysis we used the DynoMag system [13] where all measurements were carried out at 300 K. The ACS data were analysed according to a model initially developed by Raihker at al [15], where also the particle size distribution is considered [6].

RESULTS AND DISCUSSIONS

Fig. 1 show TEM images of the xanthan structure without and with integration of magnetic particles.

There are differences in coarseness of the etched structure due to how much water is etched from the gel structure. Even in the sample containing MNPs there seemed to be difference in concentration of the MNPs as seen as differences in colour of the gel. Differences in amount of MNPs are seen at lower magnification with 1000nm scale bars. There is also a difference in how etched the surface structure is as described above.



Figure 1. TEM image of the xanthan structure (top) and Xanthan structure with magnetic particles with particle mean size of 80 nm (bottom). The threadlike structures are the xanthan strands and the magnetic particles are the dark structures. The brighter areas are deeper pores not covered with contrasting platinum. Scale bars in the images are 200 nm.



Figure 3. In-phase component (top) and out-of-phase component (bottom) of ACS versus frequency of magnetic excitation field for MNPs BNF-Dextran 80 nm (left) and BNF-Dextran 100 nm (right), at different xanthan/water concentrations. The MNP iron concentration is 1 mg/ml in all prepared samples.

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Samples of different xanthan/water concentrations were prepared and mixed with MNP (iron concentration 1 mg/ml for all measurements). Fig. 2 shows ACS spectra for MNPs with mean particle size of 80 nm and 100 nm, respectively. From the ACS data we determined the viscosity and shear moduli using the viscosity/ACS model previously described [6]. The results for the MNP systems with mean particle sizes of 80 nm and 100 nm in xanthan/water concentration of 0.5 wt %, are shown in Fig. 3.



Figure 3. Viscosity (circles) and shear modulus (squares) versus magnetic excitation field frequency (in Hz) for MNPs BNF-Dextran 80 nm (top) and 100 nm (bottom), and xanthan/water concentration of 0.5 wt %.

Since the MNP system only can measure the surrounding viscoelastic properties when the particles undergo Brownian relaxation, the determined shear moduli and viscosity is only valid up to frequencies of about 10 kHz for the 80 nm particles and about 1 kHz for the 100 nm. The 100 nm relaxes with the Brownian relaxation at lower frequencies due to its larger particle size.

We can also see from Fig. 3 (in the frequency range valid up to 1 kHz for both MNP systems) that the determined shear moduli and viscosity are lower for the MNP system with particle mean size of 80 nm. This would suggest that the larger particles are more hindered in the xanthan structure.

We can also observe from the result that the determined viscosity and shear moduli agrees well with traditional oscillatory rheological measurements at higher xanthan/water concentrations for the MNP system with mean particle size of 80 nm but for the MNP system with mean particle size 100 nm the viscosity and shear modules are close to the rheological measurements even at lower xanthan/water concentrations.

CONCLUSIONS

We have measured nanorheological properties (shear modules and viscosity) of different concentrations of xanthan/water solutions using magnetic nanoparticles with different particle mean sizes of 80 nm and 100 nm.

We found that the determined shear modulus and viscosity are lower for the MNPs with mean particle size of 80 nm than compared to 100 nm particles, which implies that the larger particles are more affected by the xanthan structure.

We found that the determined viscosity and shear modulus agree well with traditional oscillatory rheological measurements at higher xanthan/water concentrations for the MNP system with mean particle size of 80 nm but, for the MNP system with mean particle size 100 nm, viscosity and shear modulus are close to the rheological measurements even at lower xanthan/water concentrations. The anticipated reason is that the size of the MNPs with 100 nm is closer to the mesh sizes in the xanthan gels.

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