



## Research articles

## Nanorheological studies of xanthan/water solutions using magnetic nanoparticles



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## ABSTRACT

We show results of nanorheological studies of different concentrations of xanthan (non-Newtonian fluid) in water using magnetic nanoparticles (MNPs) together with the AC susceptibility (ACS) vs frequency method. For comparison we also show the ACS response for different concentrations of glycerol in water (Newtonian fluid). The ACS response is measured, and the data is modelled using dynamic magnetic models and different viscoelastic models. We study the ACS response (in-phase and out-of-phase ACS components) at different concentrations of xanthan in water (up to 1 wt% xanthan) and with a constant concentration of MNPs. We use MNP systems that show Brownian relaxation (sensitive to changes in the environmental properties around the MNPs). ACS measurements are performed using the DynoMag system. The Brownian relaxation of the MNP system peak is shifting down in frequency and the ACS response is broadening and decreases due to changes in the viscoelastic properties around the MNPs in the xanthan solution. The viscosity and the storage moduli are determined at each excitation frequency and compared with traditional macroscopic small amplitude oscillatory shear rheological measurements. The results from the traditional rheological and nanorheological measurements correlate well at higher xanthan concentration.

## 1. Introduction

The complete chewing and swallowing process of food is an intricate 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 (determined by viscoelastic properties of the food) directly in the mouth generally implies using large experimental equipment, with cables connected to the sensors that interfere with the oral processing mechanisms, and especially with the perception of the food. Instead, the use of magnetic nanoparticles (MNPs) enables remote sensing of local viscoelastic properties by measuring and analyzing the dynamic magnetic response from the MNPs. This means that rheological properties, texture and aggregation could be followed remotely without using sensors in the mouth that interfere with the oral processing mechanisms. Furthermore, by modifying the particles and, for instance, embedding MNPs in proteins, information on aggregation and

food texture may be gained.

Iron oxide based MNPs are used in several biomedical applications such as in the areas of diagnosis, actuation, imaging and therapy [1,2]. Previous nanorheological studies using magnetic nanoparticles in various concentrations of PEG, gelatine and polymer melts have used AC susceptibility (ACS) measurements [3,4].

In the present study, xanthan gum is used as a model system. Xanthan gum is a microbial polysaccharide which is commonly used as food thickener. Xanthan molecules consist of a branched primary structure with a (1–4)-linked- $\beta$ -D glucose backbone with ionic side chains, which in solution behave as stiff, rod-like helices. Xanthan solutions show a thixotropic flow behaviour with a yield stress, at very low xanthan concentrations, due to the stiffness and the charge of xanthan molecules [5,6]. Xanthan molecules in solution can form intermolecular aggregates through hydrogen bonding and polymer entanglements. At concentrations at which the hindrance between the repelling rods becomes larger, the rods ‘freeze’ in random orientations

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[6]. The viscosity-concentration relationship of xanthan agrees with the theory of semidilute unentangled and semidilute entangled regimes [7]. When concentrations exceed the overlap concentration of the macromolecules, xanthan forms a physical gel.

Hereafter, we present results of nanorheological studies of solutions with different concentrations of xanthan in water (non-Newtonian fluid) or glycerol in water (Newtonian fluid) using multi-core MNPs together with the ACS vs frequency method. The results are compared with conventional oscillatory rheological measurements.

## 2. Material and methods

### 2.1. Experimental

The MNP system used in this study consists of commercially available iron-oxide multi-core particles with a mean particle size of about 80 nm (BNF, micromod Partikeltechnologie GmbH) with either starch or dextran as particle matrix material. The individual magnetic cores in the multi-core particles are in the range of 10–20 nm.

For the proposed application, i.e. food textural measurements, multi-core MNPs offer advantages over single-core MNPs: first, the magnetic moment is larger, resulting in a higher sensitivity [8]. Second, the peak of the out-of-phase component of ACS is within the frequency range of the food oral processing.

Transmission Electron Microscopy (TEM) image and hydrodynamic particle size distribution can be seen in Fig. 1. TEM was performed using a FEI Titan 80–300 equipped with a field emission gun and operating at 80 or 300 kV.

As can be seen in Fig. 1, the BNF particle system used in this study has a typical multi-core structure containing several magnetic cores per particle.

In order to use magnetic nanoparticles in rheological studies the MNPs must relax via the Brownian relaxation (e.g. particle magnetic moment locked in a specific direction of the MNP), meaning that the Néel relaxation time of the magnetic core must be longer than the Brownian relaxation time of the particle itself [9]. As determined in previous ACS measurements, the MNP system used in this study exhibits Brownian relaxation [8].

Solutions were prepared by dissolving xanthan gum in deionised water (Sigma Aldrich, MO, USA). MNPs particles were added to have final iron concentration of 1 mg/ml and xanthan concentrations in the range 0.25–1 wt%. We also prepared samples with different glycerol concentrations in water (15, 30, 45 and 60 wt%) (Sigma Aldrich, MO, USA).

From previously published electron microscopy images of xanthan networks [10], it was inferred that the average pore size in transient xanthan networks was in the range of 100 nm, almost the same size as the diameter of the MNPs. However, the dynamic nature of xanthan networks [11] makes it difficult to estimate a specific pore size, and therefore is more likely that at the concentrations used in this study, xanthan molecules create a heterogeneous network with different pore sizes.

The rheological properties of the xanthan solutions were measured at 25 °C, using an Ares-G2 (TA instruments, Waters LLC, USA) strain-controlled rheometer. A cone and plate geometry (40 mm, 0.04 rad) was used. A frequency sweep was carried out from 0.06 to 600 rad/s (0.01 to 100 Hz). The imposed strain during oscillatory shear measurements was chosen within the linear response regime.

For the ACS analysis, samples were prepared by mixing MNPs solutions in xanthan and glycerol solutions from the same batches as prepared for the rheological analysis. The samples were mixed with vortex in order to have a homogenous solution.

The ACS measurements were performed with the DynoMag system [12] (RISE Acreo, Sweden) at 25 °C. Field amplitude of the excitation field was varied between 0.1 and 0.5 mT. In the ACS method, an alternating magnetic field is applied over a sample and the in-phase (real

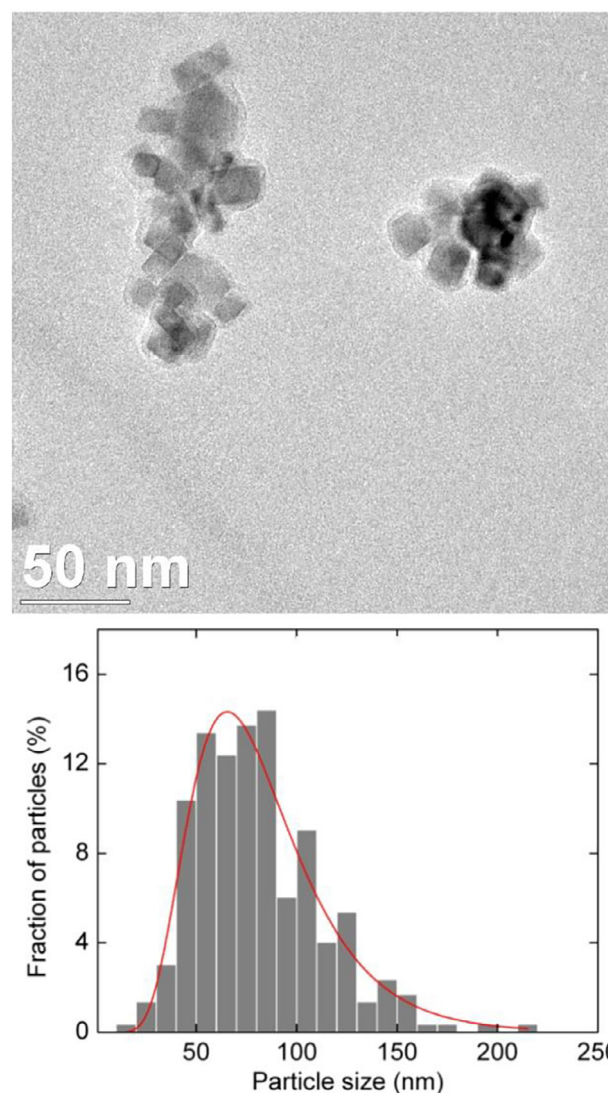


Fig. 1. TEM image showing the structure of the BNF Starch multi-core MNPs (top) and their corresponding particle ensemble size distribution (bottom).

part) and out-of-phase (imaginary part) of the AC susceptibility is determined [13].

### 2.2. Theory

The measured ACS spectra were fitted using two ACS models. One of the models is the generalized Debye model and is based on the Debye model to describe the ACS response. In the Debye model for MNPs dispersed in a Newtonian fluid (for instance water) and undergoing Brownian relaxation, the hydrodynamic particle size together with the viscosity of the fluid determine the relaxation time [13]. In the generalized Debye model, the viscosity is divided into a real and imaginary part ( $\eta = \eta' - i\eta''$ ), where the imaginary part is linked to the storage modulus in the fluid according to  $G' = \omega\eta''$ . The frequency-dependent susceptibility,  $\chi(\omega)$ , is given by:

$$\chi(\omega) = (\chi_{DC} - \chi_{high}) \int \frac{1}{(1 + i\omega\alpha r)} f(r)_{LN} dr + \chi_{high} \quad (1)$$

where  $\alpha = 4\pi r^3/k_B T$ ,  $\chi_{DC}$  is the DC susceptibility,  $\chi_{high}$  the high frequency susceptibility [14,15],  $T$  the temperature,  $k_B$  the Boltzmann constant,  $r$  the radius of the particle and  $f(r)_{LN}$  is the particle size distribution (assumed to be log-normal). The generalized Debye model can be used when the storage modulus is not too high.

A Voigt-Kelvin system is a viscoelastic system with a viscous and an elastic term in parallel. In the limit of negligible particle inertia and magnetic excitation torque,  $\chi(\omega)$  can be described by the following equation, which is based upon the model originally developed by Raikher et al. [3,16]:

$$\chi(\omega) = \frac{1}{3} \int (\chi_{||}(\omega) + 2\chi_{\perp}(\omega)) f(r)_{LN} dr + \chi_{high}, \quad (2)$$

where

$$\chi_{\alpha}(\omega) = \chi_{0,\alpha} \left( 1 + i\omega \int_0^{\infty} e^{i\omega t} F_{\alpha}(t) dt \right)$$

$$F_{||}(t) = \frac{\cosh\left(\frac{k_B T}{K} \exp\left(-\frac{t}{\tau_K}\right) - 1\right)}{\cosh\left(\frac{k_B T}{K}\right) - 1}$$

$$F_{\perp}(t) = \frac{\sinh\left(\frac{k_B T}{K} \exp\left(-\frac{t}{\tau_K}\right) - 1\right)}{\sinh\left(\frac{k_B T}{K}\right)}$$

$$\chi_{0,||} = 2(\chi_{DC} - \chi_{high}) \exp\left(-\frac{k_B T}{K}\right) \left[ \cosh\left(\frac{k_B T}{K}\right) - 1 \right]$$

$$\chi_{0,\perp} = 2(\chi_{DC} - \chi_{high}) \exp\left(-\frac{k_B T}{K}\right) \sinh\left(\frac{k_B T}{K}\right)$$

and elastic parameter  $K = 8\pi G' r^3$  and the time constant  $\tau_K = \eta'/G'$ . The symbol  $\alpha$  describes the orientations parallel ( $||$ ) or perpendicular ( $\perp$ ) to the excitation field.

In both model cases the in-phase and imaginary components of the viscosity (or storage modulus) are determined at each excitation frequency (a fitting procedure for both the in-phase and out-of-phase value of the AC susceptibility at each frequency using the FSOLVE algorithm in Matlab). After fitting the determined values of viscosity and storage modulus are included in the model and plotted against the experimental oscillatory rheological data in order to check the accuracy of the fitting.

### 3. Results and discussions

ACS measurements of the original MNP system (particles dispersed in water), using the generalized Debye model give a particle size that is in good agreement with Dynamic Light Scattering (DLS) data. From these ACS results we found that the particle size is somewhat larger (about 10%) for the particles with starch as particle matrix compared to the ones with dextran. This is compatible with the knowledge that dextran and starch have different molecular weights of 40 kDa and 200 kDa, respectively. This results in a slightly thicker polysaccharide matrix of the BNF-Starch particles compared to corresponding BNF-Dextran particles, yielding larger particle size of the MNP system with starch as particle matrix material. The fitting of these ACS data using Eq. (1) gives the size distribution that is used in the fitting of the viscosities and storage modulus for the fluids under investigation.

In the first measurements we used different mixtures of glycerol in water (Fig. 2). In this case glycerol and water mixture is a Newtonian fluid, where the storage modulus should be zero and the generalized Debye model (Eq. (1)) was used to determine the viscosity. From Fig. 2 we can see that we only have a shift in relaxation frequency and no broadening of the ACS spectra when changing the glycerol concentration.

The viscosity values determined from the ACS analysis for the different glycerol concentrations were compared to the experimental oscillatory rheological measurements and data published in Ref. [17]. As can be seen in Fig. 3, the results from the ACS analysis agree well with both experimental measurements and literature data. Similar agreement was also observed for the BNF-dextran MNPs.

The in-phase and out-of-phase components of the AC susceptibility

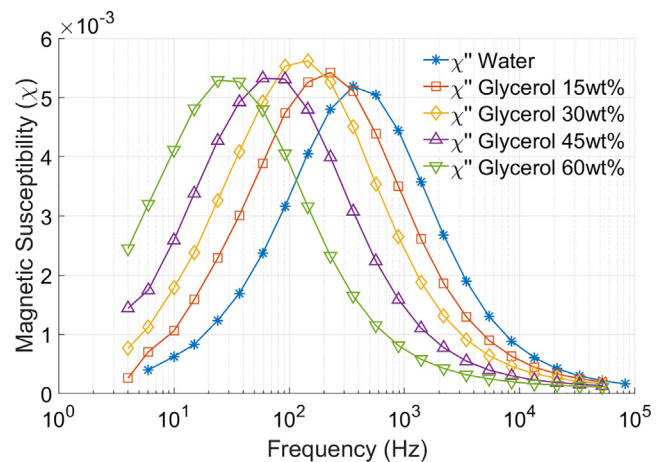


Fig. 2. Out-of-phase components of ACS for different concentrations of glycerol in water (15, 30, 45 and 60 wt%). The MNP iron concentration is 1 mg/ml for all measurements and the particle matrix material is starch.

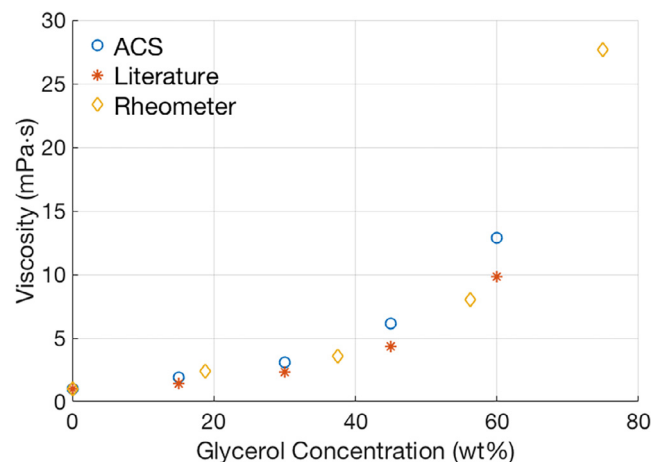


Fig. 3. Viscosity versus glycerol concentration determined from ACS analysis (using BNF starch MNP system) (circles), experimental oscillatory rheological measurements (diamonds) and literature data (stars).

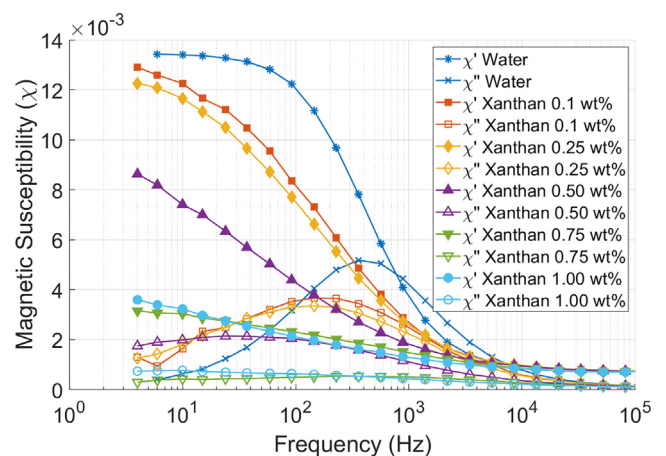
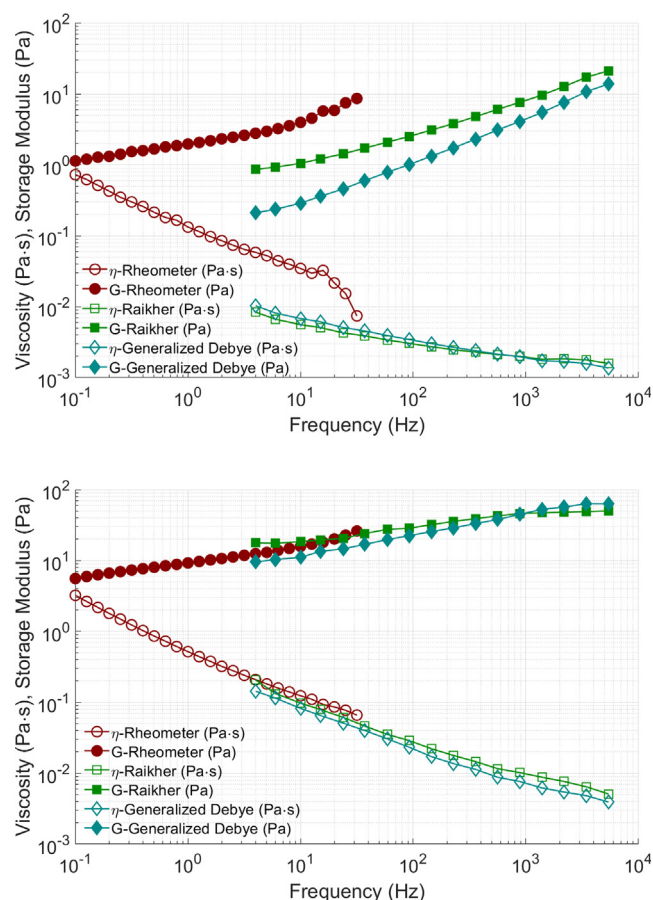


Fig. 4. In-phase ( $\chi'$ ) and out-of-phase ( $\chi''$ ) components of the ACS vs frequency for xanthan concentrations between 0 and 1 wt% in water. The MNP iron concentration is 1 mg/ml for all measurements and the particle matrix material is starch.





**Fig. 5.** Viscosity (open symbols) and storage modulus (solid symbols) versus frequency as determined by the ACS analysis (diamonds: generalized Debye model; squares: Raikher-based model) and traditional oscillatory rheological measurements (circles). Xanthan concentration is 0.25 wt% (top) and 1 wt% (bottom). The MNP iron concentration is 1 mg/ml for all measurements and the particle matrix material is starch.

versus frequency at different xanthan concentrations are shown in Fig. 4. From varying the magnetic field amplitude, we found that the results were independent on the excitation field amplitude.

From Fig. 4 we can see that we get both a shift in relaxation frequency and a substantial broadening of the ACS spectra, which is an effect of introducing viscoelastic properties [3]. We found no MNP concentration dependency in the ACS response for different xanthan concentrations.

By using the model in Eq. (2) and fitting the data (in-phase and out-of-phase components) at each excitation frequency, using the same fitting strategy as before, the viscosity and storage modulus at each excitation frequency were determined using both the ACS analysis as well as rheological measurements. The result can be seen in Fig. 5 for xanthan concentration of 0.25 and 1 wt%.

At a xanthan concentration of 1 wt%, the results from the ACS nanorheological analysis correlate well with the rheological measurements. We also observe that the generalized Debye model and the Raikher-based model both coincide with the rheometry measurements and thus could be potentially used interchangeably. However, at a xanthan concentration of 0.25 wt%, there is some deviation between the ACS analysis and rheological measurements. A similar behaviour is observed for the BNF-dextran MNPs at both 0.25 wt% and 1 wt%.

We believe that this is due to the interaction between the MNPs and the xanthan matrix, which depends on the particle size compared to the pore size of the xanthan structure that is dependent on the xanthan concentration [10,11]. We will investigate this further with different

particle sizes.

#### 4. Conclusions

We have shown that by using MNPs together with ACS analysis, it is possible to measure viscoelastic properties for both a Newtonian fluid (glycerol) and a non-Newtonian fluid (xanthan), at higher oscillation frequency compared to a traditional rheological method.

For glycerol, the viscosity obtained from ACS analysis agree well with both experimental oscillatory rheological measurements and literature data.

For xanthan, some deviation between ACS nanorheological analysis and traditional rheological measurements is observed at a lower xanthan concentration of 0.25 wt%. Increasing the xanthan concentration yields an improved agreement between the two methods. We believe that this is due to the size ratio between the MNPs and the xanthan pore size that is dependent on the xanthan concentration, which will be further investigated.

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