Nano-rheometry for food oral processing

Mats Stading[1,3], Patricia Lopez-Sanchez[1], Vincent Schaller[2], and Christer Johansson[2]

[1]Research Institutes of Sweden, Product Design and Perception, Gothenburg, Sweden
[2]Research Institutes of Sweden, Acreo, Gothenburg, Sweden
[3]Chalmers University of Technology, Industry and Materials Science, Gothenburg, Sweden

ABSTRACT

Mastication and swallowing last a few seconds, yet this food oral processing determines our complete perception of texture, taste and aroma of the product we are eating. This oral processing is an intricate combination of voluntary and involuntary actions and it involves complex flow geometry, mass transport of fluids and gases and signal processing and feedback from the brain. Any attempt of inserting measuring devices in the mouth will fail because the complete oral processing will be influenced.

We have therefore developed a remote, non-invasive determination technique using magnetic sensing and magnetic nanoparticles (MNP). A small amount of iron oxide particles senses their surrounding texture through their rotation and the nano-viscoelasticity can therefore be picked up without disturbing the oral processing.

INTRODUCTION

Eating and drinking serve two major purposes: to supply the body with sufficient energy and nutrients, and to give pleasurable sensory (=culinary) experiences. Healthy individuals apply highly unconscious but nevertheless very well coordinated strategies for the oral processing of foods and drinks with the major goal of producing easy-to-swallow boluses consisting of a mixture of the ingested food or drink and saliva. The main oral processing activities are chewing, production of saliva and transportation of the food and drink including the prepared bolus, within the mouth[1]. During the (short) time it takes to carry out these activities the receptors of various senses in the oral cavity and in the nose are stimulated[2], and ideally, this stimulation gives rise to pleasurable food experiences.

An important experience is texture. Local viscoelastic properties can explain part of the textural perception, and the dynamic viscosity reflects the fluidity of a fluid food and complex modulus reveals the mobility in a solid product. By measuring and anlysing the dynamic magnetic response from MNPs in the food, the stochastic Brownian relaxation of the MNPs can be determined and the local nano-viscoelastic properties can be calculated from the Brownian relaxation time.

Suitable MNPs consist of iron oxide. Iron is an essential trace element and the recommended daily intake is 9mg (15mg for fertile women)[3]. Iron-oxide is also an approved additive in many food products (E172). Current magnetic measurement techniques require 0.1-1 µg/ml which would amount to 0.1-1 mg iron oxide in e.g. 1 l of milk.

MNPs have been subject of extensive research since 1930 when a single-domain particle was defined as a particle with all its spins in the same direction, i.e. with only one direction of magnetization. Typically, any spherical magnetic core below about 100 nm (MNPs) is in such a state. MNPs are already applied in the areas of biomedical applications diagnosis, therapy, actuating, imaging and now in food science[4,5].

MNPs with larger magnetic cores show Brownian relaxation (rotation)[4] and it is possible to detect this relaxation by measuring the dynamic magnetic response. The Brownian relaxation is determined by the viscosity around the MNP on a nano-scale. For MNPs dispersed in water at room temperature the magnetic cores must be larger than about 18 nm in order to exhibit Brownian relaxation. This kind of MNP systems can be purchased from many companies or synthesized in labs using stable synthesis routes.

By measuring and analyzing the dynamic magnetic response from MNPs in the food, the stochastic Brownian relaxation of the MNPs can be determined and the local nano-viscoelastic properties (dynamic viscosity η) can be calculated from the Brownian relaxation time τ_B according to:

$$\eta = \tau_B k_B T/3V, \qquad (1)$$

where T is temperature, V the hydrodynamic particle volume and k_B Boltzmann's constant. In a real MNP system there is always a distribution of particle size and the viscoelastic properties are then determined by using dynamic magnetic modelling of the experimental determined data[6].

Dynamic magnetic measurements give information of the relaxation properties of the MNP system and can be used to determine the Brownian relaxation time and thereby the viscosity around the MNPs. A time varying magnetic field is applied over the MNP system and the dynamic response is measured with a highly sensitive AC susceptometry (ACS) instruments. The frequency is varied, and the response is measured at each frequency.

In the current study we have utilised magnetic nano-particles of iron-oxide to determine the nano-rheology of three systems ranging from Newtonian glycerol over viscoelastic xanthan solutions to gelation of alginate.

MATERIALS AND METHODS

Glycerol (Sigma Aldrich, MO, USA) was mixed with deionized water to give concentrations 15, 30, 45 and 60 wt%.

Xanthan (Sigma Aldrich, MO, USA) was dissolved in deionised water at 1% w/w. MNP particles (80 nm, BNF, Micromod Partikeltechnologie GmbH, Rostock, Germany) were added to give 1 mg/ml concentration.

Alginate was used in the form of alginic acid (Sigma Aldrich).

The rheological properties were measured at 25 °C, using an ARES-G2 rheometer (TA Instruments, Waters LLC, USA). A cone and plate geometry (40 mm, 0.04 rad) was used.

Gelation of alginate was monitored at 117 Hz in a concentric cylinder system. The strain during oscillatory shear measurements was always chosen within the linear regime.

The AC susceptometry (ACS) measurements were performed with a DynoMag system[7] (RISE Acreo, Sweden) at 25 °C. Field amplitude of the excitation field was varied between 0.1 and 0.5 mT.

RESULTS AND DISCUSSION

Three model systems of increasing complexity were used to evaluate the nan-rheologial properties determined by ACS. Aqueous glycerol is a Newtonian fluid and the viscosity was determined by viscometry using the Ares G2 as a reference for the ACS measurements. As previously reported the generalized Debye model yielded a local viscosity which corresponded well with the viscometric measurements as well as with literature data[8] (Fig 1). The particle size distribution required for the model fitting was also acquired by ACS of the MNPs in water.

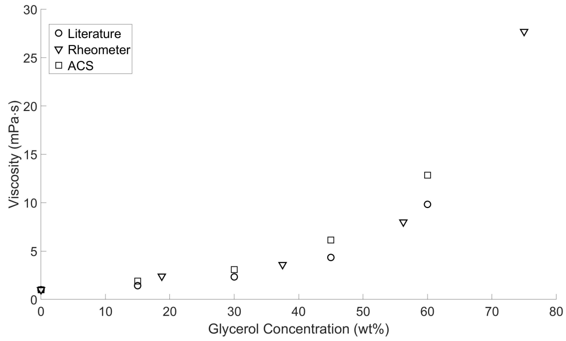

Figure 1. Viscosity of glycerol at increasing concentration measured by rheometry, AC susceptometry as compared to literature data[8].

Solutions of xanthan are viscoelastic fluids one step more complex than the Newtonian glycerol solutions. Different models were used to calculate the viscosity from the ACS measurements and the Raikher model was found to give the most accurate overlap with small-angle oscillatory shear (SAOS) measurements[2, 8]. Fig. 2 shows rheometry data and the nano-rheological data using the Raikher model. The data overlaps well. It is also worth noting that the two methods together covers a broad range of frequencies.

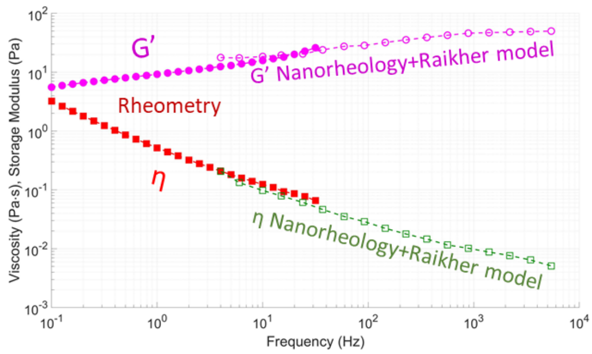

Figure 2. Viscosity η and storage modulus G' of a 1% w/w xanthan solution determined by rheometry and AC susceptometry.

During food oral processing rheological properties will change over time due to mixing, particle size reduction, increased content of saliva and enzymatic action. This means that the nano-rheological method must be able to resolve rheology over time. A suitable system for validation is therefore gelation where a solution changes from a low viscosity, low modulus solution to a solid gel. The gelation can be triggered by e.g. chemical crosslinking or temperature induced physical crosslinks.

Alginate gels at room temperature on addition of calcium ions. The cross-linking reaction is very fast and in order form a homogeneous gel a slow leaching system of calcium carbonate and glucono-delta-lactone was used. The effect on the magnetic susceptibility is shown in Fig. 3 were the peak in X" shifts to lower frequencies and broadens on gelation. The shift is typical for an increase in viscosity and the broadening indicates increased elasticity.

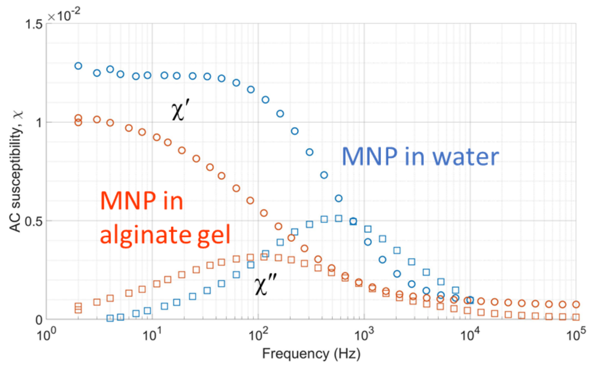

Figure 3. AC susceptibility of magnetic nano-particles (2 mg/ml) in water and in a 1% alginate gel.

CONCLUSIONS

Magnetic nano-rheology corresponds well with rheometry for Newtonian and viscoelastic fluids as well as for monitoring gelation of an alginate gel. Successful measurements depend on the choice of MNP type and size the size needs to be large enough to interact with the elements of the structure responsible for the rheological response, yet sufficiently small to capture the Brownian relaxation.

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REFERENCES

1. Chen, J. (2009) "Food Oral Processing – A Review", Food Hydrocolloids, **23**, 1-25

2. Foster, K.D., Grigor J.M.V, Cheong, J.N., Yoo M.J.Y, Bronlund, J.E and Morgenstern, M.P. (2011), "The Role of Oral Processing in Dynamic Sensory Perception", *J. Food Sci.* **76**, R49-R61

3. Livsmedelsverket, the Swedish National Food Agency, available at livsmedelsverket.se

4. Pankhurst, Q.A., Connolly, J., Jones, S.K. and Dobson J., (2003) "Applications of magnetic nanoparticles in biomedicine", *J. Phys. D: Appl. Phys.* **36**, R167–R181

5. Caoa, M. et al. (2012) "Food related applications of magnetic iron oxide nanoparticles: Enzyme immobilization, protein purification, and food analysis", *Trends Food Sci. Techn.* **27,** 47e56.

6. Bogren, S *et al.* (2015) "Classification of Magnetic Nanoparticle Systems—Synthesis, Standardization and Analysis Methods in the NanoMag Project", *Int. J.Mol.* Sci. **8**; 16:20308-20325

7. F. Ahrentorp, J. Blomgren, C. Jonasson, A. Sarwe, S. Sepehri, E. Eriksson, A. Kalaboukhov, A. Jesorka, D. Winkler, J.F. Schneiderman, M. Nilsson, J. Albert,

8. T. Zardán Gómez de la Torre, M. Strømme, C. Johansson (2017) Sensitive magnetic biodetection using magnetic multi-core nanoparticles and RCA coils, *J. Magn. Magn.Mater.* **427**, 14–18.

9. Sriviriyakul, T., Bogren, S., Schaller, V., Jonasson, C., Blomgren, J., Ahrentorp, F., Lopez-Sanchez, P., Berta, M., Grüttner, C., Zeng, L., Stading, S. amd Johansson, C. (2018) "Nanorheological studies of xanthan/water solutions using magnetic nanoparticles", *J. Magnetism. Magn. Mater.*, **473**, 268-271

10. Raikher, Y.L., Rusakov, V.V., Coffey, W.T., Kalmykov, Y.P. (2001), "Dynamic susceptibilities of an assembly of dipolar particles in an elastic environment", *Phys. Rev. E,* **63**, 031402.