Interfacial behavior of casein-inulin interactions at the oil and water interfaces

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Abstract. Mixtures of proteins and dietary fiber are frequently used in many technological applications in food industry. In many of these applications' protein-dietary fiber mixtures are used in the production of processed dispersions containing two or more immiscible phases such as aqueous, oil and/or gas phases in the forms of emulsions or foams. Due to their large interface areas, the dispersions are spontaneously unstable systems and prone to destabilization. The instability of these systems is achieved by a protective surface layer around the particles. The properties of this interface layer are controlled by the composition and structure of the adsorbed material. The aim of present study is to investigate the interfacial properties of protein- dietary fiber interactions at oil/water interfaces. For this reason, 1% solutions of casein, as a model compound, and mixed with the inulin, an important dietary fiber, have been prepared. The BiCone rotor has a diameter of 68 mm and a cone angle of 10° was used and the data were recorded at 25℃. The rotational as well as oscillatory experiments were conducted and the interfacial shear stress (τi), interfacial viscosity (ηi) and interfacial modulus (Gi', Gi'') values were recorded. Water and oil interfacial properties of samples were evaluated in terms of time, stress, strain and frequency sweep measurements. The Gi' values were higher than Gi'' (Gi'> Gi'') at studied frequency and the ηi was measured 1.616x10-3 Pas.m at the shear rate of 100.

INTRODUCTION

Proteins are commonly used amphiphilic molecules which widely find applications in food dispersions such as foams and emulsions. In contrast to small molecule surfactants, proteins not only reduce the interfacial tension during adsorption, they can also form a viscoelastic (multi) layer in the interface to protect oil droplets against flocculation and coalescence (Wang et al., 2011).

Dietary fibers which is mostly provided by the cell wall of vegetables, fruits and cereals, include polysaccharides (pectin, cellulose and hemicellulose) and lignins. Both soluble and insoluble fibers may be present; however, higher amounts of

insoluble fibers are used for food fortifying purposes (Staffolo, Bertola, & Martino, 2004). The fiber may interact with other food components during processing. These interactions can lead to changes in the bioavailability of nutrients, texture or flavors of the product (Fernandez-Garcia & McGregor, 1997). Due to providing a desired structure to the foodstuffs, biopolymer mixtures are widely used in the food industry. Protein-polysaccharide complexes formed by electrostatic interactions have been reported to increase the stability of emulsions (Roudsari, Nakamura, Smith, & Corredig, 2006; Tran & Rousseau, 2013).
Therefore, the knowledge of mechanisms occurring in casein-polysaccharide mixture systems is of great importance (Bourriot, Garnier, & Doublier, 1999a). Casein micelles have a relatively large and highly complex structure (diameter 20-600 nm). This molecular assembly is a supramolecular association of individual casein subunits of αs1- , αs2- , β- and κ-caseins. These fractions are organized in miscelles according to hydrophobic and hydrophilic groups (Bourriot, Garnier, & Doublier, 1999b).

The interfacial rheology describes the functional interaction of the deformation of an interface, the forces exerted on it, and consequently the flows in the adjacent phases of the fluid. This can be determined by applying dilatation and shear forces. The shear rheology of the interfacial layers at the gas/liquid or liquid/liquid phase boundaries is related to a wide range of technical applications, especially in colloidal systems including large interfaces such as foams and emulsions. The interfacial flow behavior of such systems is controlled by the presence of particles present in the system such as proteins, surfactants, lipids, which will be occurred due to the adsorption of interfacial active molecules and attachment of particles or by spreading or layer formation of the amphiphilic substances. The application of shear deformations to the interface layers provides indirect access to inter-and intra-molecular interactions in the interfaces (Krägel & Derkatch, 2010). In the interface rheology, the interface area is kept constant and the information about the elastic or storage module (G') and the viscous or loss module (G'') depends on the frequency (Krägel & Derkatch, 2010; Oliveira, Santos, Vieira, Fraga, & Mansur, 2017). The BiCone geometry, magical rod and the du Noüy ring was used for the measurement of the surface shear rheology and various proteins such as β-lactoglobulin and hydrophobins have been studied using these attachment (Li et al., 2016). However, there are few studies on the interfacial rheology of proteins and dietary fibers and their interactions at oil/water interfaces. The interfacial rheology of casein which is the major fragment of the milk protein and the inulin as a dietary fiber was used to investigate the interfacial viscoelastic behavior adsorption layer at the water and oil interfaces using a rotational rheometer equipped with BiCone geometry.

MATERIAL AND METHODS

The inulin used in this study was kindly purchased from the Orafti Food Ingredients (High performance inulin, HP, Belgium), the casein from bovine milk was from Sigma-Aldrich, USA. The sunflower oil was purchased from a local market.

The aqueous phase of samples was prepared with the equal amount of inulin and casein. The total of these two ingredients in the mixture was 1%. After weighing and preparation of aqueous phase, the samples were subjected to continuous stirring for 12 h on a magnetic stirrer.

Interfacial rheology for the determination of the effects on sunflower oilwater interface was studied with a peltier system rheometer (Haake Mars II, Karlsruhe, Germany) with BiCone probe (BC 68 / 5Ti). Before starting the analysis, the micro stress calibration, device and probe calibration was conducted carefully. The liquid form (water), which had a high density and which would be at the bottom, was filled up to the specified line spacing and the gap height was determined for the device. As a result of this measurement, data manager system was opened and curve fit of Fn against h values was plotted. The zero-crossing point x0 was calculated and used as the measuring gap for the rheological measurements at interface layer. Dynamic shear interfacial rheology analyzes were performed with time sweep, frequency sweep and strain sweep tests. The time sweep test was performed with amplitude value of ω = 0.1 %, angular frequency γ = 1 rads-l 1 for 1 hour. The frequency sweep test was run at γ= 0.1–10 rads-1 and ω=0.1% linear region. The strain sweep test was conducted at ω= 0.01-100% and γ= 1 rads–1 (Baldursdottir, Fullerton, Nielsen, & Jorgensen,2010)

For both rotational as well as oscillatory test the measured raw data was modified in a such way that the contributions from the two bulk fluids are subtracted from the total results. The following equations was used for the calculation of the Gi' and Gi'' of the sample.

$$Gi' = G'total(\omega) - \frac{G'_A(\omega)}{2} - \frac{G'_B(\omega)}{2} \qquad (1)$$

$$Gi'' = G''total(\omega) - \frac{G''_A(\omega)}{2} - \frac{G''_B(\omega)}{2} \qquad (2)$$

where

$G_i'(\omega)$ is interfacial storage modulus as a function of the applied angular frequency

$G_i''(\omega)$ is loss modulus as a function of the applied angular frequency

G'total (ω) is the total storage modulus signal from the measurement with two liquids and interfacial layer as a function of the applied angular frequency

G''total (ω) is the total loss modulus signal from the measurement with two liquids and interfacial layer as a function of the applied angular frequency

GA'(ω) is total storage modulus from the bulk fluid A

GB'(ω) is total storage modulus from the bulk fluid B

GA''(ω) is total loss modulus from the bulk fluid A

GB''(ω) is total loss modulus from the bulk fluid B

RESULT AND DISCUSSION

In order to investigate the effect of inulin and casein interaction at the oil/water interface, time sweep test were conducted and the elastic modulus (Gi'), loss modulus (Gi'') and interfacial complex viscosity (ηi*) were measured at a frequency of 1 rads-1 and a strain amplitude of 0.1 % as shown in Figure 1. Moreover, the time evaluation of Gi' and Gi'' of the sample was illustrated in Figure 1. The value along with the variation in the Gi'' was larger than that of Gi'. Also, the interfacial complex viscosity increased during the time sweep experiment. The structure and conformation of the casein-inulin may support viscoelasticity and interfacial adsorption. In a previous study, it has been reported that protein-polysaccharide systems exhibit stronger dilatational viscoelastic properties than protein alone (Jourdain, Schmitt, Leser, Murray, & Dickinson, 2009).

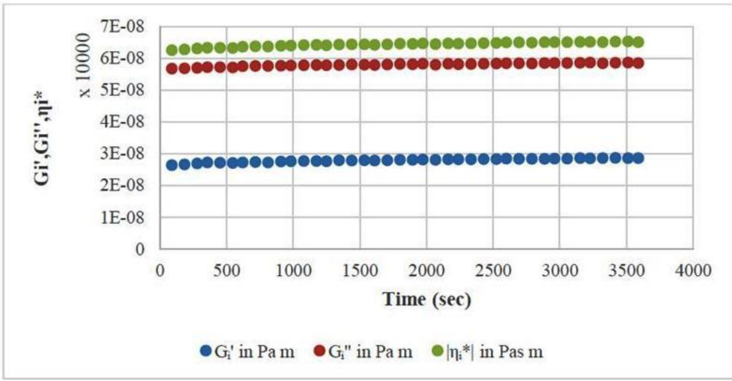

Figure 1
Time evaluation of the interfacial elastic modulus (G_i'), viscous modulus (G_i'') and interfacial complex viscosity (η_i*) of the sample at oil/water interface

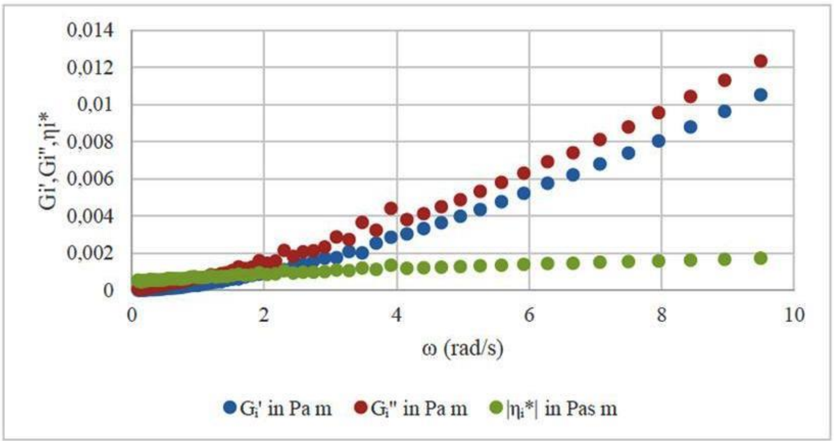

Figure 2
Frequency sweep experimental results of samples at the oil/water interfaces

Frequency sweep test was performed at 25℃, γ=0.1% and the 0.1-10 rads-1 frequency range and the results were illustrated at Figure 2. Both the elastic and viscous interfacial modulus of the casein-inulin at oil water interfaces was found to be dependent on the frequency, over the measured frequency range unlike the interfacial complex viscosity. While the η_i* of the sample was independent of the frequency, the G_i'and G_i'' values of the sample was increased as the applied frequency was increased. The prepared sample was exhibited viscous behaviors with the G_i''>G_i' at studied frequencies.

Strain sweep measurements were performed in order to trace the possible fracture mechanism of the samples. Figure 3 exhibited the strain dependence of the both interfacial elastic modulus and interfacial viscous modulus of the samples studied at the oil and water interface.

As can be easily seen from this figure, linear trend except some of the data was observed in the G_i' and G_i'' values of the casein and inulin samples at the measured frequency. G_i'' values were over the G_i'. The presence of dietary fiber may had an influence on the conformation of the casein molecules at the oil and water interface. In previous study, it is also reported that the presence of polysaccharides may hinder the conformational changes β-conglycinin at the oil/water interface, thus leading to a delay in reaching the adsorption rate (Li et al., 2018). The results of this study indicated that the dietary fiber and protein interaction may affected the interfacial rheological properties of the emulsions at oil and water interfaces. It should be considered that the film formation and emulsion stability of food products could be attributed to these results.

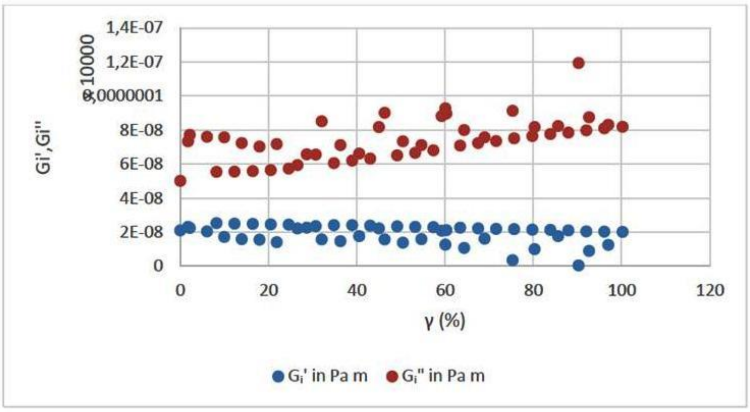

Figure 3
The strain dependency of elastic and viscous modulus of caseininulin at the oil/water interface

CONCLUSIONS

In this work, the interfacial rheological properties of casein and inulin at oil and water interface has been studied. Shear, time and frequency sweep measurements with the aid of BiCone geometry was done in order to characterize the samples. The results suggested that interfacial shear rheological properties may strongly affected by the dietary fiber and protein interaction. Besides, this study indicates that protein and dietary fiber may significantly improve the emulsifying and rheological properties of inulin-casein samples and provides useful information for the preparation of high emulsifying food products.

REFERENCES

Baldursdottir, S. G., Fullerton, M. S., Nielsen, S. H., & Jorgensen, L. (2010). Adsorption of proteins at the oil/water interface—Observation of protein adsorption by interfacial shear stress measurements. *Colloids and Surfaces B: Biointerfaces, 79*(1), 41-46.
Bourriot, S., Garnier, C., & Doublier, J.-L. (1999a). Phase separation, rheology and microstructure of micellar casein–guar gum mixtures. *Food Hydrocolloids, 13*(1), 43-49.
Bourriot, S., Garnier, C., & Doublier, J.-L. (1999b). Phase separation, rheology and structure of micellar casein-galactomannan mixtures. *International Dairy Journal, 9*(3-6), 353-357.
Fernandez-Garcia, E., & McGregor, J. (1997). Fortification of sweetened plain yogurt with insoluble dietary fiber. *Zeitschrift für Lebensmitteluntersuchung und-Forschung A, 204*(6), 433-437.
Jourdain, L. S., Schmitt, C., Leser, M. E., Murray, B. S., & Dickinson, E. (2009). Mixed layers of sodium caseinate+ dextran sulfate: influence of order of addition to oil− water interface. *Langmuir, 25*(17), 10026-10037.
Krägel, J., & Derkatch, S. R. (2010). Interfacial shear rheology. *Current opinion in colloid & interface science, 15*(4), 246-255.
Li, W., Wang, Y., Zhao, H., He, Z., Zeng, M., Qin, F., & Chen, J. (2016). Improvement of emulsifying properties of soy protein through selective hydrolysis: Interfacial shear rheology of adsorption layer. *Food Hydrocolloids, 60*, 453-460.
Li, W., Wang, Y., Zhao, H., He, Z., Zeng, M., Qin, F., & Chen, J. (2018). Effects of soluble soy polysaccharides and gum arabic on the interfacial shear rheology of soy β-conglycinin at the air/water and oil/water interfaces. *Food Hydrocolloids, 76*, 123-130.
Oliveira, P. F., Santos, I. C., Vieira, H. V., Fraga, A. K., & Mansur, C. R. (2017). Interfacial rheology of asphaltene emulsions in the presence of nanoemulsions based on a polyoxide surfactant and asphaltene dispersant. *Fuel, 193*, 220-229.
Roudsari, M., Nakamura, A., Smith, A., & Corredig, M. (2006). Stabilizing behavior of soy soluble polysaccharide or high methoxyl pectin in soy protein isolate emulsions at low pH. *Journal of agricultural and food chemistry, 54*(4), 1434-1441.
Staffolo, M. D., Bertola, N., & Martino, M. (2004). Influence of dietary fiber addition on sensory and rheological properties of yogurt. *International Dairy Journal, 14*(3), 263-268.
Tran, T., & Rousseau, D. (2013). Stabilization of acidic soy protein-based

dispersions and emulsions by soy soluble polysaccharides. *Food Hydrocolloids, 30*(1), 382-392.

Wang, L., Xie, H., Qiao, X., Goffin, A., Hodgkinson, T., Yuan, X., Fuller, G. G. (2011). Interfacial rheology of natural silk fibroin at air/water and oil/water interfaces. *Langmuir, 28*(1), 459-467.