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Reconsidering the importance of interfacial properties in foam stability

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ABSTRACT

In food industry, protein isolates are often used to help in the formation and stabilisation of food foams. Subsequently there is great interest in (1) understanding the effect of processing parameters on the functional properties of the isolate, and (2) methods and techniques that can help to predict the foam properties. This article describes the foaming properties of proteins that were modified in the Maillard reaction. From these relatively simple experiments results were obtained that indicate that for certain protein solutions the foam properties can vary significantly, while the interfacial properties are constant.

Commercial protein isolates originate from only a few sources, mainly egg white and whey, and sometimes plant proteins (e.g. soy). Despite these limited sources a large variety of isolates with a wide range of properties is produced. One source of variation is the isolation procedure, but at least equally important are the conditions used before, during and after drying the protein solution to form the dry powder.

From the literature it was found that one of the major changes to the protein during processing of the isolates is the covalent coupling of sugars via the Maillard reaction. To study the effects of these reactions, a model system was produced that consists of proteins that were glycated to different degrees using Maillard reaction. For each sample, interfacial properties (e.g. surface pressure, dilatational modulus) were determined, and foam experiments were performed. The results show that at constant concentration of both the protein (0.5 g/L) and sugar (0.7 g/L), the foam-ability and stability could be significantly improved (e.g. non-modified lysozyme does not foam, the highest modification is easily foamed and the foam has a half-life time of 200 s).

Interestingly, the improved foam properties could not be related to any change in interfacial properties. While foam stability improved with increasing modification, the measured interfacial properties were not significantly affected. These observations seem to go against the general view that changes in foam behaviour should be reflected in changes in the interfacial properties. Additional experiments on thin liquid films were performed, where the disjoining isotherm was measured. These isotherms did not show significant differences in the interactions between the adsorbed layers. This indicates that the electrostatic and steric interactions between the adsorbed layers do not depend on the degree of modification. Only the thin film stability against rupture was found to increase with increasing modification. The thin film experiments lead to the hypothesis that aggregates (or oligomeric proteins) formed during modification might become trapped in the film. The presence of these oligomeric proteins could result in an increase of the apparent viscosity in these films, or in gelling or jamming of the liquid phase between the two interfaces. In other words, the observed behaviour is the result of the confined geometry of the thin films.

The results confirm other observations that Maillard reactions improve foaming properties. Moreover, strong indications were found that to predict foam stability we need more than the traditional parameters (i.e. (dynamic) surface pressure, interfacial reology, and disjoining pressure).

1. Introduction

The control of foam formation and stability is important in a wide range of food applications [1]. The foam properties of food systems are often adjusted by adding protein isolates. Isolates are mainly produced from egg (egg-white), or milk (whey), although sometimes proteins from plant origin are used. Despite

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the small number of sources, a large variety of different isolates is commercially available. Each isolate has its own typical foaming properties. The differences result from the isolation procedure, but more importantly from the conditions used before, during and after the drying process [2–6]. For instance, egg-white powder is heated for a period of 3 days at 80 °C to increase its foaming properties [2,5,7]. For the development and optimisation of new protein isolates (for instance from plant origin) it is important to improve the current understanding of the functionality of protein isolates and the role of processing conditions.

Different processing steps are involved in the drying of the protein solution [8]. These processing steps affect the protein state and lead to such changes as: decreased solubility [6], aggregation [8–10], and Maillard reactions [4,5]. From these, Maillard reactions seem to be important, since it has been shown to lead to aggregation, and aggregation typically leads to loss of solubility [11–17]. In addition, Maillard reactions have been shown to affect the foam and emulsifying properties of proteins, although the mechanism appears to be unclear [11,18–20]. It is important to note that the term 'Maillard reaction' actually covers a wide set of reactions. The first and major part of the Maillard reaction is the covalent coupling of the reducing end of a sugar to a free amino group (mostly from lysine residues) of a protein. Subsequent reactions can lead to formation of a wide range of products, including brown-coloured components and flavors. For more information on the reactions that occur we refer to the work of van Boekel [21].

Based on the above, it was decided to study the mechanism by which Maillard reactions affect the foam properties of proteins. To this aim, Maillard reacted protein variants were produced from lysozyme, ovalbumin and β-lactoglobulin (Lys, Ova, and Blg respectively) and by two different methods (with Lys). From these relatively simple experiments we hope to improve the understanding of protein foam stability on two levels. For the application of protein isolates, the relation between chemical structure and composition of proteins and foam stability is studied. Additionally, a nice set of samples is obtained to observe the extent to which interfacial properties can be used as predictors for foam-ability or foam stability. The latter will improve the understanding of proteins foams on a more fundamental level.

2. Materials and methods

2.1. Chemicals

Chicken egg lysozyme (L-6876) from Sigma was used without further purification (with samples from different batches similar results were obtained, results not shown). Ovalbumin was isolated as described previously [22], with the only adaptation that the protein was eluted with 0.15 M NaCl. Bovine β-lactoglobulin was isolated and purified from fresh cow milk as described by de Jongh et al. [23]. Ortho-phthaldialdehyde (OPA) and 2-(dimethylamino)ethanethiol hydrochloride (DMA) were also purchased from Sigma.

3. Production of glycated protein variants

To allow an overview of the effects of mild glycation[1] of proteins on foam properties the glycation was performed with different methods and with different proteins. Firstly, lysozyme (Lys) was modified in dry-state and in solution. This is illustrated in Fig. 1, where also the names for these samples are shown as they will be used in the rest of the text. Secondly, ovalbumin (Ova) and β-lactoglobulin (Blg) were modified in solution, to assess how the observed effects of glycation depend on the proteins used.

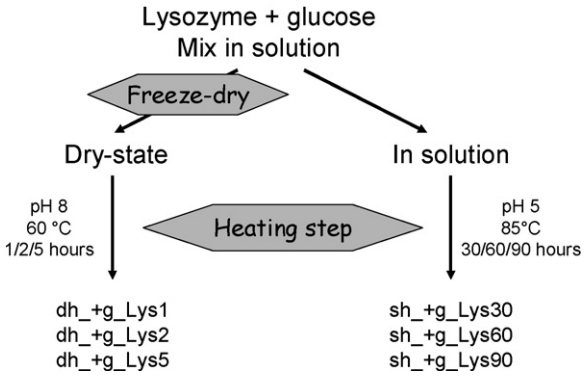

Fig. 1. Production scheme of glycated variants of lysozyme by heating in dry-state or solution.

3.1. In dry-state

The glycation in dry-state was performed under the conditions described by Broersen et al. [24]. Lysozyme (2 g) and glucose (2.78 g) were dissolved in 200 mL demineralized water. This solution has a protein concentration of 10 mg/mL and a molar ratio of free amino groups:glucose of 1:16. The pH of the solution was adjusted to 8.0 using 1 M KOH followed by freezing and freeze-drying. The freeze-dried mixture was incubated at 60 °C at a relative humidity of 65% (equilibrated atmosphere using a saturated $NaNO_2$ solution) for 1, 2 or 5 h. After reaction the samples were extensively dialyzed against demineralized water at a temperature of 4 °C and finally freeze-dried and stored at −18 °C.

3.2. In solution

The concentrations used for heating in solution were chosen (1) to have the same ratio between free amino groups and glucose as in the dry-state modification, and (2) to obtain the protein concentration that can be directly used in the foam experiments. The protein (0.5 mg/mL) and glucose (0.695 mg/mL) were dissolved in sodium acetate buffer (10 mM, pH 5.3). Samples were heated in a water bath at 85 °C for 30, 60 or 90 min. The sample solutions were stored at −18 °C, without any further treatment.

For Ova and Blg the used pH (5.3) is too close to the iso-electric point of the proteins. Therefore these proteins were dissolved and heated in a 10-mM phosphate buffer at pH 7.0. For these proteins, the concentration of glucose was adjusted to keep the same molar ratio of free amino groups to glucose (1:16). For reference, for each sample a reference was heated in the absence of sugar (for same heating times). For information, the heating temperature of 85 °C is well above the denaturation temperature of Lys [25], Ova [26], and Blg [25] (74, 78 and 80.8 °C respectively).

4. Characterization of degree of modification

4.1. Matrix assisted laser desorption/ionization time-of-flight mass-spectrometry (MALDI-TOF MS)

The molecular weight distributions of the modified proteins were measured on a Voyager-DE™ RP (PerSeptive Biosystems, U.S.A.), as described by Broersen et al. [24], using 3,5-methoxy-4-hydroxy cinamic acid as a matrix.

[1] Glycation is the general term for non-enzymatic coupling of sugars to proteins, which is the first step in the Maillard reaction. The enzymatic coupling of sugars to proteins is commonly referred to by the term glycosylation. Since our interest is in very mildly treated samples, we prefer to refer to the Maillard reacted variants as glycated variants.

5. Characterization of physical properties

After production of the modified protein variants, several experiments were performed to assess the changes in interfacial and foaming properties. The typical protein concentration used was 0.5 g/L. At this concentration the viscosity of the solution is not affected. In addition, similar concentrations are commonly used in the literature. For the lysozyme variants the experiments were performed in 10 mM sodium acetate buffer pH 5.3, for Blg and Ova pH a 10-mM phosphate buffer at pH 7.0 was used.

5.1. Single interface properties

5.1.1. Automated drop tensiometry (ADT)

The ADT (ITConcept, France) was used to measure the development of interfacial pressure and visco-elastic modulus of the interface as a function of time, using the conditions as described by Wierenga et al. [27]. The dilatational rheological properties were measured using a deformation of the area with 7% at a frequency of 0.1 Hz. In other experiments the frequency was varied (0.01–1.5 Hz). It was found that rate of deformation did not affect the observed differences between the samples.

5.1.2. Ellipsometry

A combined setup of a multi-skop ellipsometer (Optrell, Germany) and Langmuir trough (Riegler and Kirstein, Germany) was used as described earlier [27]. For these samples the values of the refractive indices of air (1.0) and protein solution (1.3327) as well as the refractive index increment ($dn/dc = 0.18$) were used.

5.2. Foaming

5.2.1. Foam beaker

Foam was formed by sparging. The beaker (radius 3.1 cm, height 13 cm) was screwed on top of a metal bottom, with a metal frit as separator. On the metal frit a square grid of small pores is made (inner diameter 0.02 mm, spaced at 0.85 mm intervals) to allow the passage of gas. For each measurement fresh solution (60 mL) was placed in the beaker, and N_2 was sparged through the solution (through the metal frit) at a flow rate of around 100 mL/min, until the foam height reached 12 cm. After the gas flow is stopped, the foam height is recorded as a function of time. To correct for minor differences in actual initial foam height, the relative foam height is calculated by dividing foam height at $t = t$ by foam height at $t = 0$. This fixed foam height is used because foam stability was found to depend on the original height of the foam [28]. The foam half-life time ($t_{1/2}$) is the time in which the foam height decreased to half its original value. All samples were measured at least in duplicate. For samples that did not reach the 12 cm mark, the maximum foam height reached was marked. The foam stability of these samples was determined by foaming in a foam tube with inner diameter 2 cm, to a height of 30 cm (liquid level at start was 10 cm) and measuring the time of total collapse of the foam.

5.3. Thin liquid film properties

5.3.1. Capillary cell

Thin films formed in a capillary cell were observed under reflected light, using the setup described previously [29–32]. The intensity of the reflected light is used to calculate the film thickness. Additional information on the technique and obtained results is given by others [33–35]. The current experiments were performed to study the drainage rate and equilibrium thickness of films formed in closed cell. In the closed cell experiments the atmosphere was in equilibrium with the sample solution that was placed in the bottom of the cell, thereby preventing evaporation of water from the thin film. Drainage was determined from films that were made without dimples. In other experiments, small liquid lenses (dimples) were purposely trapped in the centre of the film during formation to observe the 'mobility' of the dimple.

Table 1
Values for the average molecular weight and average number of glucose molecules per protein after modification as determined by MALDI-TOF MS.

	Molecular weight (kDa)	# Added glucose molecules
NM-Lys	14.3	0
dh_+g_Lys 1	15.1	5
dh_+g_Lys 2	15.7	9
dh_+g_Lys 5	16.1	11

5.3.2. Porous cell

The porous cell used in this study was coupled to a pressure sensor and a capillary. A syringe connected to the capillary was used to adjust the pressure in the films. This setup was described first by Mysels and Jones [36] and later by Dimitrova et al. [31]. As in the capillary cell experiments the thickness of the film was measured from the intensity of reflected light. By simultaneous measurement of pressure in and the thickness of the film, the disjoining pressure isotherm was determined.

It may be clear that once the solution is placed in the film holder, adsorption starts. To assure that all experiments were performed under similar condition, the time between placement of solution and start of the measurement was approximately the same (1 min).

6. Results

6.1. Lysozyme: glycation in dry-state versus in solution

6.1.1. In dry-state

Lysozyme was heated in dry-state in the presence of glucose for 1, 2 and 5 h. For these samples the degree of glycation was determined by matrix assisted laser desorption ionisation time-of-flight mass spectrometry (MALDI-TOF MS, see Table 1). After 1 h of heating an average of 5 glucose molecules per protein were detected. The degree of modification increased to 11 glucose molecules per protein for 5 h heating. In addition to the covalent coupling of glucose molecules, subsequent reactions occurred as was evident from the colouring of the samples.

The characterization of the interfacial properties was started by determining the adsorption kinetics by ellipsometry (see Fig. 2). For all times, the measured adsorbed amount for all three modified variants was similar. Therefore only the average values are given in the figure. It is important to note that we do not compare to

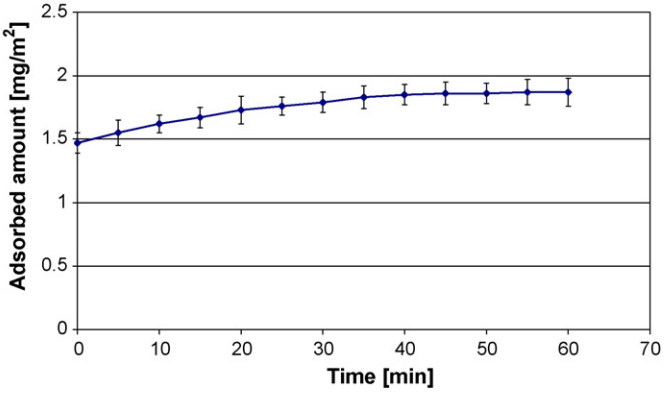

Fig. 2. Adsorbed amount as a function of time for dg_+g_Lys. The curve shown is the average for all modifications (1, 2, 5 h); the error bars illustrate the small variation between the samples.

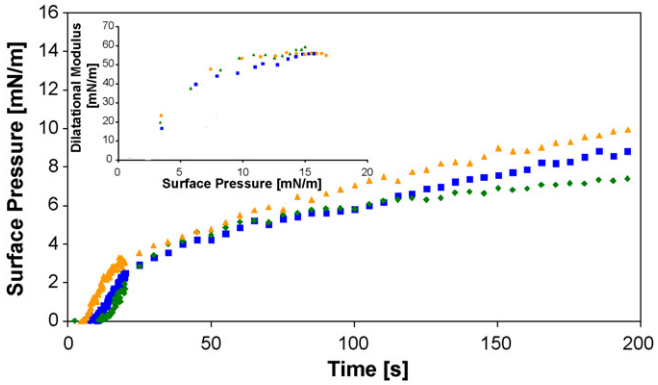

Fig. 3. Surface pressure as function of time for dry-state glycated lysozyme variants (□) 1 h, (△) 2 h, and (◊) 5 h heating); inset shows dilatational elastic modulus versus surface pressure for the same samples.

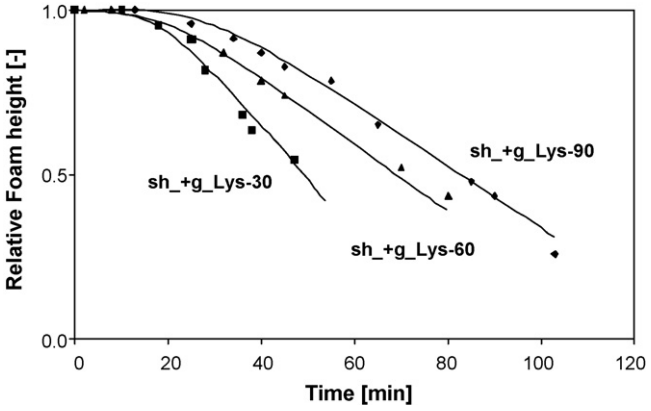

Fig. 5. Decay of foam height in time for glycated lysozyme variants (heated in solution).

the native, or non-treated lysozyme. The data are not shown, but under these conditions the adsorption rate of non-treated lysozyme is much smaller than the modified variants. The development of surface pressure that results from adsorption was measured as a function of time (see Fig. 3). For all three samples (dh_+g_Lys1, 2 and 5), a short lag-time is observed (10 s), after which the surface pressure increases to reach a value of around 8 mN/m after 200 s. As for the adsorbed amount, the development of surface pressure was for all three samples similar within the experimental error. That the heating time does not affect the observed surface pressure is further supported by the results obtained with the other proteins as will be discussed later (Fig. 7). Additionally, no significant differences were found in the relation between the dilatational modulus (E_d) versus the surface pressure (Π, see inset of Fig. 3). From the equality of the $E_d - \Pi$ relation, it follows that the adsorbed layer reacts similar to the deformation. Whether one assumes desorption or rearrangement processes to occur, or that this relation reflects the equation of state, in all cases it must be concluded that the adsorbed layers of the different variants demonstrate the same behaviour. This, in combination with the similar adsorption kinetics leads to the conclusion that there are no significant differences in the properties of the adsorbed molecules. In addition, one would normally assume these samples to demonstrate similar foam behaviour, since both the interfacial properties and the bulk properties (concentration, pH, ionic strength, viscosity) are similar.

In contrast to the very similar interfacial properties of the variants, large differences in the foam properties were found. Initial foam tests with these samples showed that at a concentration 0.5 g/L the dh_+g_Lys1 did not form any foam, but the higher modified samples did. When the concentration was increased to 3 g/L all variants formed foam (4, 6 and 10 cm respectively for dh_+g_Lys1, 2 and 5), but still not enough to reach the 12 cm mark. These samples were then foamed in a smaller tube, where 30 cm foam was formed and the time for total collapse of the foam was recorded. The collapse times for the 3 variants is shown in Fig. 4A. There is a clear increase in foam lifetime (from about 5 to 25 min).

6.1.2. *In solution*

From the dry-state glycation of lysozyme interesting results were obtained. To test if similar effects could be obtained by a different method of modification, lysozyme was modified by heating in solution in the presence of glucose. Since the interest was first to study interfacial and foaming properties the chemical characterization of these samples is not part of the current manuscript. The variants obtained had improved foam-ability, and for these samples the foam height was measured as a function of time (as described in Section 2) and the foam half-life time was taken as indicator for the foam stability. Results are shown in Figs. 4B and 5. As for the dry-state samples, the foam stability increased with increasing time of modification ($t_{1/2}$ increases from about 1 to 6 min). As a reference, the native, or non-treated lysozyme does not foam at all. If lysozyme is heated in the absence of glucose it still has poor foam-ability and foam stability. This shows that the glycation has significant impact on the foam properties of lysozyme. Further support for this comes from the fact that both methods of glycation lead to increased foam stability with increasing modification (although the foam from sh_+g_Lys is less stable than dh_+g_Lys).

After observing the improvement of foam properties for lysozyme in two different methods it was decided to test the effect of glycation for two more proteins in one method. From the modification of ovalbumin and β-lactoglobulin in solution and comparison with the lysozyme heated in solution it can be established whether the effect of glycation is specific to the protein, or a generic result of the modification.

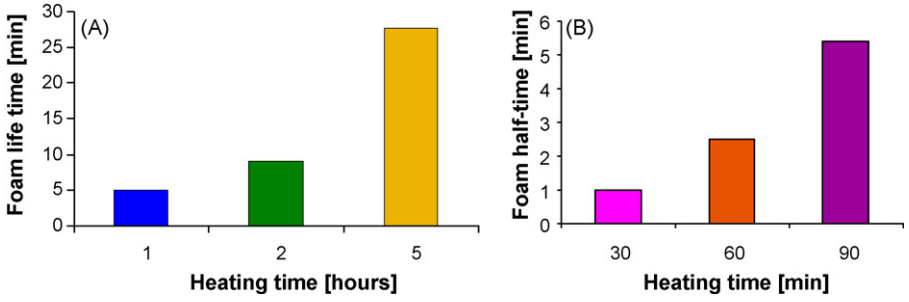

Fig. 4. Foam life time and foam half-life time for glycated lysozyme in (A) dry-state and in (B) solution.

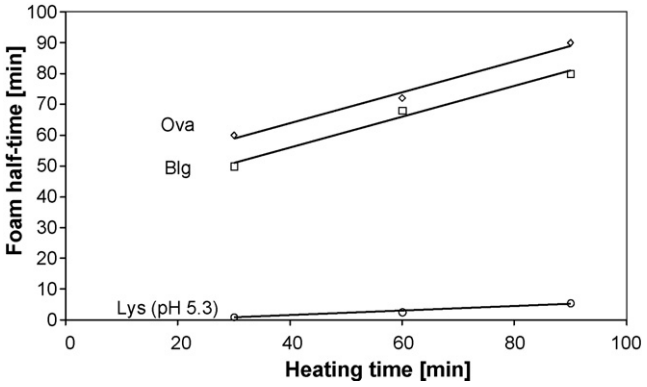

Fig. 6. Foam stability (half-life time) as a function of heating time for different proteins; heating in solution in presence of glucose.

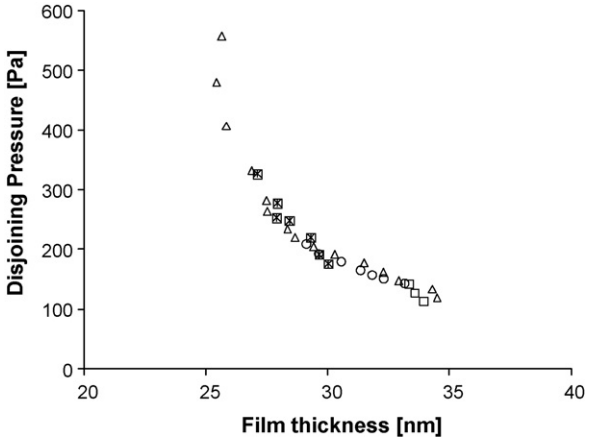

Fig. 8. Disjoining pressure isotherms for dh_+g_Lys variants.

6.2. Lysozyme versus Ova and Blg

Ovalbumin and β-lactoglobulin were modified with the same conditions used for lysozyme, except that the pH was set at 7.0 to avoid extensive aggregation (since the p*I* of these proteins is 5.2 and 4.8 respectively). The foam stability of the glycated variants was measured and $t_{1/2}$ is plotted versus the modification time in Fig. 6. For all three proteins an increase of the foam stability is observed after heating in the presence of sugar. In the absence of glucose longer heating times were found to result in lower values for the foam stability (data not shown).

For all glycated variants the surface pressure and dilatational modulus were measured during adsorption. The results are shown in Fig. 7A–C. For each protein, no effect of heating time is observed on either the surface pressure kinetics, or the dilatational rheology.

6.3. Thin liquid film properties

The proteins that were heated in the presence of glucose showed marked improvement of foam properties with increasing heating times, but little or no effects on the properties of the adsorbed layer at the air–water interface. However, it may be offered that the foam stability is dominated by the stability of the thin liquid films between bubbles against rupture or coalescence. Therefore thin liquid films were studied in the porous cell and in the capillary cell. In the porous cell, the disjoining pressure was measured as a function of the applied pressure. The measured disjoining pressure (the pressure needed to keep the film at certain thickness) is the result of the attractive and repulsive interactions between the adsorbed layers. In Fig. 8 the disjoining pressure isotherms for the sh_+g_Lys1,2 and 5 are given. The data for all 3 samples fall on the same curve. This indicates that at the interactions (steric, electrostatic, van der Waals) between the interfaces are identical for all 3 samples. Surprisingly, neither the single interface properties (surface pressure), nor the disjoining pressure isotherm provide any information that explains the differences in foam stability. To find more information, the drainage behaviour and dimple mobility of thin liquid films were studied in the capillary cell.

As shown in Fig. 9, a dimple formed in a film of native lysozyme leaves the film within the first seconds after formation. This behaviour is typically associated with low-molecular surfactants. For the lowest degree of modification (dh_+g_Lys1) the dimple is still mobile, but it leaves the film only at longer times. The lower dimple mobility in glycated samples becomes more clearly visible for the samples with longest heating time (2 and 5 h). For the dh_+g_Lys5 the dimple remains stable in the middle of the film, and disappears only over a period of around 300 s. These observations were repeatable and are thus considered significant. The dimple mobility was the only parameter that showed clear and significant differences between the modified variants. It is an indication that the mobility of liquid and dissolved molecules in the film is different for the different samples. This will be discussed in more detail in the next section.

7. Discussion

The starting point for the presented study is the observation that commercial protein isolates can vary in foam functionality while their chemical composition (i.e. protein content) is constant. In addition, reports in the literature indicated that Maillard reactions may occur in these samples and that they can improve foaming properties. To study the effect of Maillard reactions, lysozyme was modified by heating for three different heating times in the

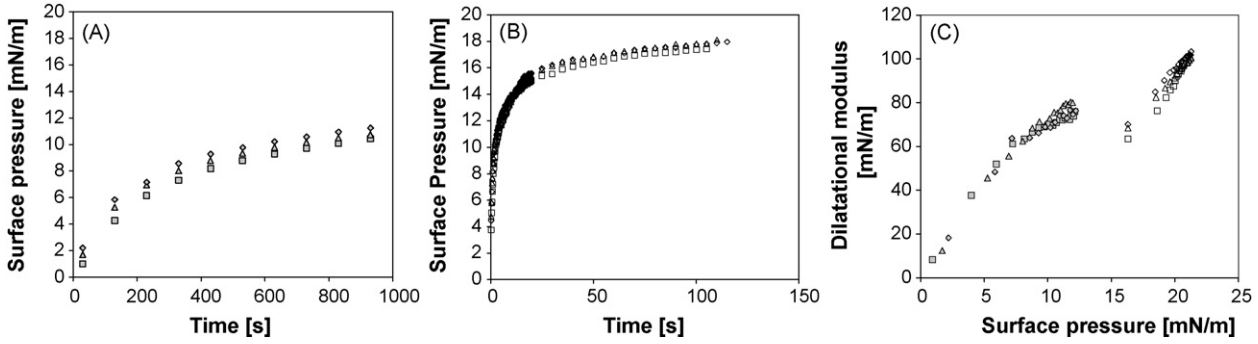

Fig. 7. Surface pressure kinetics for modified Ova (A) and Blg (B) variants, and the dilational modulus as a function of surface pressure (C), (□) 30 min; (△) 60 min, and (◊) 90 min heating.

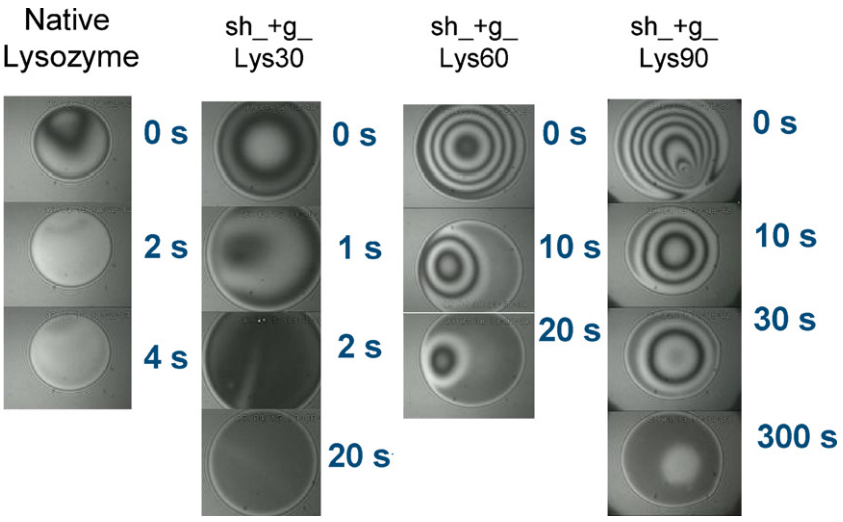

Fig. 9. Images from thin films made in the capillary cell, showing the dimple behaviour of native and glycated variants of lysozyme.

presence of glucose in dry-state or in solution. For both methods of modification, longer heating times resulted in increased foam stability. Control experiments confirmed that the improvement of the foam properties was not merely an effect of the heating of the protein: lysozyme heated in the absence of glucose did not form any foam at all. Moreover, the modification of ovalbumin and β-lactoglobulin in solution yielded similar results. This shows that the effect of modification is generic and not specific for lysozyme.

These results show that indeed a wide range of foam properties can be obtained (at constant protein concentration) depending on the degree at which Maillard reactions have occurred.

However, these experiments yielded a far more interesting and surprising observation. This observation came from the measurement of the interfacial properties of the modified protein variants. Before discussing these results and their consequences, we will shortly discuss the relevance of interfacial properties. In food industry there is a need for methods and techniques to predict the macroscopic properties of foam in different formulations or systems. Typically such predictions are based on micro- and mesoscopic system parameters as illustrated in Fig. 10. In the following the general view on foam formation and stability will be described shortly here, further information can be found in several articles [37–44]. The solution contains a certain concentration of proteins, which in time adsorb to the air–water interface to form an adsorbed layer. The adsorbed layer changes the physical properties of the interface. These changes are characterized by such parameters as the adsorbed amount, surface pressure, or elastic modulus (in dilatation or shear). When two bubbles are close together, additional phenomena can become important. The thickness of the film separating the bubbles decreases as a result of drainage. The rate of drainage depends on the bulk and interfacial viscosity. The equilibrium thickness of the film depends on the capillary pressure and the disjoining pressure. The disjoining pressure isotherm describes the decrease in film thickness that results from the force applied on the film. It is commonly assumed that rupture occurs once a film reaches its 'critical' thickness. The rupture of the thin films leads to coalescence and subsequent decrease in foam volume.

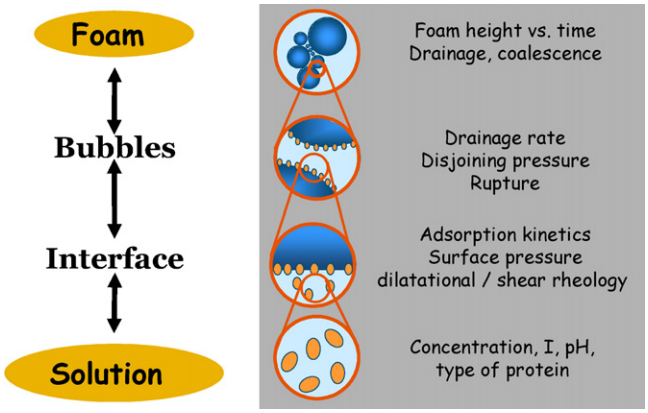

Fig. 10. Typical scheme to explain the stabilisation of foam by adsorption of proteins or surfactants from the solution to the air–water interface.

It may be clear from the above that any change in foam properties is expected to be accompanied by changes in the interfacial properties. In this respect, the results obtained in this study are quite surprising. For each sample-set studied, it was found that the longer heating time did not result in any significant changes of surface pressure, or dilatational elasticity. For the dry-state heated lysozyme samples more elaborate experiments were performed. From ellipsometry it was found that the adsorbed amount (as a function of time) was also identical for the dh_+g_Lys samples (1, 2 and 5 h heating). The dilatational experiments were performed at different frequencies (0.01–1.5 Hz), but for all heating times similar values were found for the complex modulus. Also the real and imaginary parts of the modulus did not depend on the heating time. From the above it may be clear that there are really no detectable differences between the adsorbed layers formed from glycated lysozyme samples with different heating times. Also the surface shear rheology did not depend on the heating time. Even the disjoining pressure isotherm was found to be nearly identical for these latter samples.

None of the above described experiments showed any significant differences between samples with longer heating time. This leads to the conclusion that no differences in the composition or the structure of the adsorbed layers exist. Therefore, based on the available data-set it was concluded that the composition and structure of the adsorbed layers formed was similar for protein variants within each treatment set. At the same time, the foam properties were improved.

As described in the start of this section, the general consensus in the field of relatively wet protein foams is that the stability of these systems should in one way or the other be reflected by the properties of the adsorbed layer. In this respect, our observation of not one, but four different sets of proteins that disobey this rule is rather unexpected. Currently, the authors feel that the observed results could be attributed to the presence of protein aggregates

(or oligomers) in the thin liquid films. It has been found by others that some aggregation may be induced during the conditions used for Maillard reaction. Such oligomeric proteins could form an ordered structure, or increase the apparent viscosity in the thin films, which would change the dynamic properties of the film. Evidence for this is given by the decreased mobility of the dimple (with longer heating time) in the capillary cell experiments of dry-state glycated lysozyme. Since the viscosity is a dynamic factor, it would not be measured in the disjoining pressure isotherm. The effects of the protein oligomers is then due to the specific geometry of the thin films. For surfactants systems it has been found that the stratification is due to ordering of micelles in the thin films. This ordering is induced by the dimensions and conditions of the thin film and is therefore not observed in the bulk solution.

Currently experiments are conducted to identify the physical parameters and mechanisms that affect the foam stability. In addition, experiments are performed to identify and characterize the aggregation state of proteins in the glycated samples.

Despite the relative simplicity of the system surprising results were obtained. It seems that for these systems, the typical interfacial properties do not lend themselves for prediction of foam properties. The fact that these observations were obtained with two different heating methods and three different proteins indicates that the underlying mechanism may be important in other systems as well. This is expected to have implications for industrial practice, and both experimental and theoretical scientific work.

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