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RHEOLOGY OF THE WET SURFACTANT FOAMS AND BIOFOMAS – A REVIEW

WŁAŚCIWOŚCI REOLOGICZNE PIAN CIEKŁYCH WYTWARZANYCH NA BAZIE SYNTETYCZNYCH SURFAKTANTÓW ORAZ BIOSURFAKTANTÓW – PRZEGLĄD

Abstract

The rheology of foams is a difficult subject due to the complexity of their structure and the nature of their components. It's influenced by multiple factors including: liquid bulk properties, gas properties, air phase volume, liquid volume fraction, solution viscosity, interfacial thin film visco-elasticity, bubble size distribution, and bubble shape. A nature of the adsorbed surfactants or biosurfactants and state of adsorption layer also modified the properties of the thin liquid film. The physical measurements of foam rheological properties are also complicated by its inherently unstable nature. Therefore, this review is focused on rheological studies and comparisons between various surfactant based foams and biofoams having well-characterized and different properties.

Keywords: *rheology*, *foams*, *surfactants*, *biosurfactants*, *proteins*, *viscoelasticity*, *yielding*

Streszczenie

Reologia układów pianowych jest skomplikowanym zagadnieniem badawczym ze względu na ich złożoną strukturę. Wpływają na nią wielorakie czynniki, takie jak: właściwości fazy ciekłej i gazowej, objętości fazy gazowej i ciekłej, lepkość roztworu, lepkoelastyczność cienkiego filmu pianowego, rozmiar i rozkład pęcherzyków gazowych. Właściwości powierzchniowo-aktywne surfaktanta lub biosurfaktanta i ich stopień adsorpcji również modyfikują parametry otrzymywanego cienkiego filmu pianowego. Fizyczny pomiar właściwości reologicznych pian jest również rzeczą skomplikowaną ze względu na ich niestabilną naturę. Z tego powodu tematem tego artykułu jest przegląd i porównanie różnych reologicznych badań dotyczących pian surfaktantowych oraz biosurfaktanowych o różnych, dobrze scharakteryzowanych właściwościach

Słowa kluczowe: *reologia*, *piany*, *surfaktanty*, *biosurfaktanty*, *proteiny*, *lepkoelastyczność*, *plastyczność*

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1. Introduction

The applications of foams are based on the large specific surface, the small specific weight and mechanical properties, depending on the applied stress. Foams exhibit linear viscoelastic behaviour when they are subjected to small shear stresses while they flow like viscous liquids when the applied shear stress is large enough to trigger bubble rearrangements [1–7]. The origin of foam elasticity comes from the deformation of bubbles from a perfectly spherical shape, in order to increase their packing density. The energy stored during the deformation increasing the surface energy and is also responsible for the viscoelastic properties of foams, their specific geometry of films, Plateau borders and vertices in the limit of dry foams.

All of these features are important in applications where foams are used to transport particles [3], i.e. in various kinds of froth flotation, in oil industry where foams are used as drilling fluids or in technology of hydraulic fracturing technology of shale gas extraction. In this context, as well as from a fundamental point of view, it is important to develop a constitutive rheological law, predicting the relation between macroscopic stress, strain and strain history. Moreover, the rheological study of the interface in foams can determine how the dispersed phase resists to deformation, or even coalescence.

The biofoams could be used in those applications in place on surfactants based foams [8–10]. Recently published papers clearly present that foams can also be stabilized by nano-particles, without surfactant or by proteins or other surface-active bioplymers. Proteins or polysaccharides received a special attention from scientific, technological and environmental points of view. Since proteins are known to form films with high interfacial elasticity and viscosity, via various forms of cross-linking that can occur between the adsorbed molecules, it might be expected that proteins would be the ideal candidates for preventing foam disproportionation thought the interfacial elastic mechanism.

In order to fully characterize the foam to allow the comparison with the theoretical models descriptions, the bubble diameter, liquid volume fraction and the solution surface tension have to be known [2, 4, 6, 7]. It is necessary to understand how the foam rheology (elasticity, viscosity and yielding) depends on the foam components (surfactants, liquid and gas) and on the parameters describing the surfactant adsorption on the thin liquid film layer. Changing the surfactants has an impact not only on the surface tension, but also modifies the properties of the lamellae thin liquid film via the variation of the degree of surfactant adsorption on the interface. The solution viscosity may also have influence on the shear rate dependence. It is still not clear how the viscoelastic properties depend on the chemical formulation (surfactants, mixtures with polymers, etc). Literature of subject report experimental results for very limited surfactant and a few proteins based systems. The importance of the nature of gas used for foaming should be also mention here. Gases soluble in water, like air or N_2 give less stable foams then less soluble gases, like C_2F_6 because the air or nitrogen diffusion through the lamellae film is faster.

2. Foam structure – drainage, coarsening and disproportionation

Foam is an extremely complex system with a cellular internal structure, in which the polydispersed bubbles are separated by thin, plane-parallel liquid films, stabilized by surfactant adsorption layers [1–4]. To produce foam the gas phase needs to be dispersed in liquid phase into bubbles. The structure and geometry of dry foam was first described by the 19th century scientist Joseph Plateau [1, 11]. It was experimentally shown that the lamellae thin films in dry foam always meet at edge (Plateau border) at angle of 120 degrees. The four borders of those lamellae films meet in a symmetrical tetrahedral vertex at angle 109.47 degrees.

Foam formation occurs always under dynamic conditions so the equilibrium adsorption coverage is rather not attained there. It can strongly affect the magnitude of the forces stabilizing the foam films. Therefore foams are inherently difficult to study systems because they are transient and the study is essentially restricted to the observations of dynamic system evolution. Owing to the size of the bubbles, which varies from fractions of a millimetre to several centimetres, foams are classified as coarse dispersion systems. In European Union foam is classified as a soft matter, while in United Stated is included for complex fluids. Production of foams involves the generation of a liquid thin film surrounding the gas bubble and a packing of gas bubbles into an overall structure. The generated foam may persist for a reasonable length of time without collapsing into separate constituent phases. However, from a thermodynamic viewpoint, foams are unstable dispersions by their very nature and should break into individual component phases in the direction of decreasing total surface free energy. The effects of the disjoining pressure, of surface elasticity and viscoelasticity, structural forces and possible effects of steric repulsions are the main parameters to be responsible for the foamability and foam stability. Foams irreversible evolve with time (ageing process).

The main processes taking places in wet foams are a free drainage from lamellae and Plateau borders, coalescence and disproportionation [1–4]. By drainage, we are referring to the irreversible flow of liquid through the foam, induced by the influence of gravitational acceleration, viscous force and pressure exceeded between the adjacent bubbles. As a result the liquid accumulate at the bottom part of foam and a global liquid content decrease within the foam. In the upper part of the foam the "dry foam" is formed with the polyhedral bubbles with thin edges. While the bubbles in the bottom part of the foams are still spherical.

When the liquid films between the bubbles are very thin, they may eventually break. The merging of two bubbles as a result of the rupture of the film between them is known as coalescence. Larger bubbles appear in the foam and the number of bubbles decreases. If this continues, the whole foam collapses.

Disproportionation (known also as a coarsening or an Oswald ripening) is described as inter-bubble gas diffusion. As a result of gas diffusion larger bubbles grow at the expense of smaller bubbles. Smaller bubbles shrink and may finally disappear. The driving force is the Laplace pressure, which for a spherical bubble is inversely proportional to its radius: $\Delta P = 2\sigma_T/r$, where σ_T is the interfacial tension and r is the bubble radius. As a result of foam ageing, the average bubble diameter was found to grow with the time elapsed since foam production following a parabolic law. The characteristic coarsening time was described [12] as a function of the bubble deformation, gas diffusivity and solubility constants, function of the liquid content, thin film thickness, bubble initial diameter and the solution surface tension.

It is clear that all destabilization (ageing) mechanisms are occurring simultaneously (see Fig. 1). Therefore the various methods, such as a conductivity or fluid drainage rate, are used for qualitative description of each of those processes. All these coupled ageing processes affected the elasticity properties as they respectively changed the distribution of the liquid and gas phase (liquid and gas volume fraction) and bubble size. The increases in the gas fraction due to drainage tend to raise the yield stress, whereas increases in the bubble size (coarsening) leads to a reduction in the yield stress [2]. Therefore they alter seriously the macroscopic (textural and rheological) properties of foams.

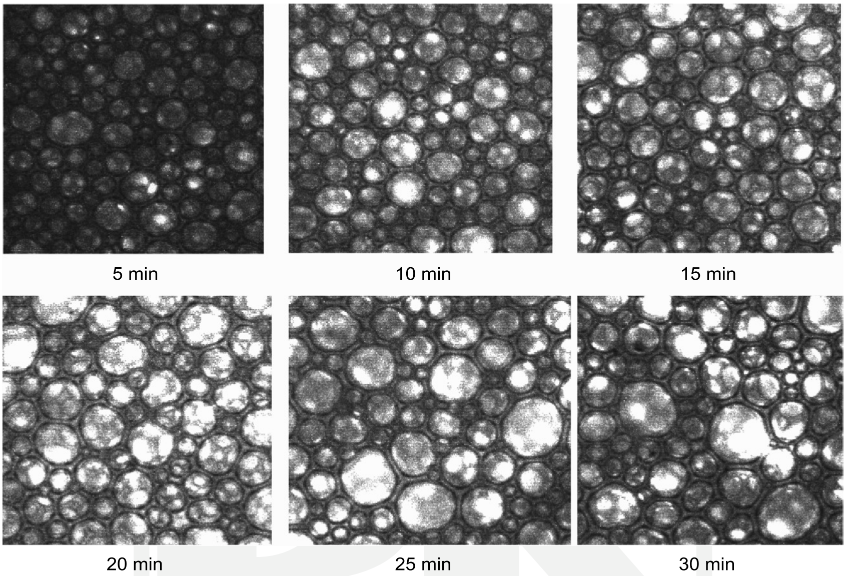

Fig. 1. Process of ageing in Nivea commercial shaving cream

Rys. 1. Proces stężenia się piany otrzymanej z komercyjnej pianki do golenia Nivea

3. Surfactant and biopolymer foams – the various ways of thin film layer stabilizations

It is generally accepted that the presence of surfactant is necessary for foam formation and stability. There is a minimum concentration of surface-active molecules necessary for foam generation. In the case of detergents, this concentration is associated with a surface coverage of the bubbles and corresponds to the inflection point on the adsorption isotherm curve [2–4].

However, there were recently published papers showing that foams can also be stabilized by nano-particles, without surfactant or by proteins or other surface-active biopolymers.

Proteins or polysaccharides received a special attention from scientific, technological and environmental points of view. Proteins are complex molecules with unique properties, which determine the life in our planet. From their easy biodegradation and natural recycling, proteins raise a motivation for using them in various industrial applications.

The relatively non-specific foaming of denatured proteins is commonplace and widely exploited in food technology [8, 13–15], the simplest examples are whipped cream and foam with whites eggs. Proteins are the most ubiquitous surface active polymers in nature. The spontaneous adsorption of proteins from solution to the air/aqueous interface is a central importance to their foaming performance [16–18]. Surface active biological macromolecules like proteins and polysaccharides can adsorb at the almost every interface and they form highly stable films contributing to stability of membranes, foams, emulsions and dispersions in general. Since proteins are known to form films with high interfacial elasticity and viscosity, via various forms of cross-linking that can occur between the adsorbed molecules, it might be expected that proteins would be the ideal candidates for preventing disproportionation via the interfacial elastic mechanism.

During foam formation proteins diffuse from the aqueous phase and adsorb at the air-water interface due to the compatibility of their hydrophobic groups with the hydrophobic character of the interfaces [13, 19]. During adsorption, protein molecules can unfold to a certain degree and reorient at the interface with polar groups exposed towards water phase and the non-polar groups towards the air phase. Protein adsorption is thermodynamically favourable due to the simultaneous dehydration of the hydrophobic portions of the protein. Hydrophobic patches of proteins surface initially drive this process, and surface hydrophobicity has been correlated with improved foaming properties. Once contacts are made with the interface, natural flexibility within the molecules can expose previously hidden hydrophobic part to the interface, potentially leading to interfacial denaturisation of the molecules. This in turn, leads to the decrease of the interfacial tension and to the formation of more or less stable interfacial protein films. The casein molecules adsorb at the gas/solution interfaces, and form elastic and rigid film with average thickness of the order of a few hundreds of nanometers. The protein molecules aggregated in a jellified matrix, making the film quite non-uniform in texture and thickness. The adsorption rate of proteins, as the most important factor for foam formation, depends on the protein concentration, the molecular weight and the structure of the proteins used. Foaming properties of proteins are influenced by a large number of parameters including thermal or chemical pre-processing conditions, method of foaming, whipping time and the physical and chemical properties of the proteins as well as the environmental factors like ionic strength or pH [20, 21]. The effect of pH on proteins is usually explained by the net charge of the molecules and the protein conformation. The final protein conformation results not only from internal interactions between the amino acids side chains, but also from their interactions with water molecules. It was shown that the Bovine Serum Albumin foam apparent poor foamability is counterbalanced by relatively large stability in 2D system of Hele-Shaw cell [22]. The foam was almost solidified. Even as a continuously thinning of the foam films was observed, the bubbles kept the nearly same shape and size on photos recorded immediately after stop of the flipping procedure and 5 minutes later (Fig. 2) [23]. The size and shape of the foam bubbles were stable as far as the foam exists. The foam collapsed only due to the film leaking. The effect was probably caused by network of adsorbed and denaturised proteins in the foam film, which solidified the cell structure, not prevent the film drainage.

One must distinguish polysaccharides that are not surface active, which includes most natural ones, from chemically modified polysaccharides that are surface active. The polysaccharides foams exist in the literature of subject mostly as a solidified foam gel materials (produced as a gas dispersion from the hydrogel) [24, 25], a resin foams [25], a polymerised foams or a dry foams [26] (foams frozen or dried). Once dispersed in water polysaccharides they have the property to increase bulk viscosity and improve stability against coalescence. The most common polysaccharides used for confectionary products are guar gum, xanthan gum and k-carrageenan [27–29].

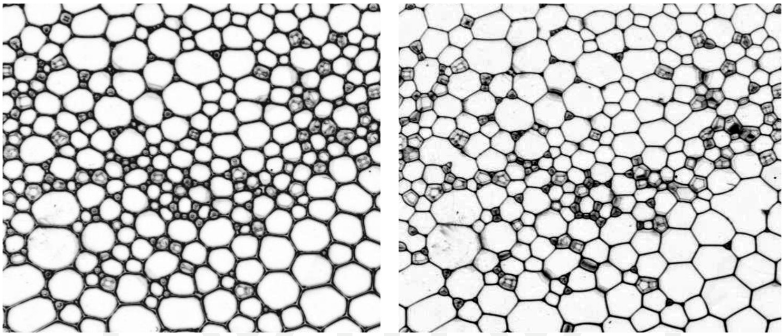

Fig. 2. Photos of Bovine Serum Albumine foams freely ageing foam in Hele-Shaw cell. Snapshots of a foam taken just after foam formation (left photo) and after long term drainage (5min – right photo) [23]

Rys. 2. Zdjęcia piany otrzymanej z roztworu Bovine Serum Albumine starzejącej się w celi Hele-Shaw. Klatki pokazują pianę od razu po wytworzeniu (lewe zdjęcie) oraz po długim czasie wyciekania (5min – prawe zdjęcie) [23]

Relatively little is known about what happens when both surface active biopolymers (proteins and polysaccharides) will be present together [29, 30]. Any lipids or other low molecular-weight surfactants present will probably adsorb to the polysaccharides nanoparticles and change their contact angle and adsorption characteristics. Proteins will adsorb to almost any type of surface, often with high affinity, and may therefore do the same. In addition, the interfacial coverage is likely to be dominated by the proteins or low molecular-weight surfactants, since the particles will adsorb more slowly due to their slower mass transport. Mixed protein - polysaccharide multilayer films may have improved properties in terms of colloidal stabilization, encapsulation and controlled release in food and pharmaceutical applications. The presence of a polysaccharide in the foaming solution can modify the interfacial and foaming properties of the protein and impart desired characteristics to a product. In particular, if there is a synergistic interaction between protein and polysaccharide, drainage and disproportionate may thus be further retarded. In addition, if the continuous phase of the protein stabilized foam could gel, interesting characteristics related to foam stability and texture properties should arise.

4. Foam generation

Foams properties varied with the method and equipment using for their preparation [2–4, 31–34]. Aqueous foams with controlled and reproducible properties are not easy to produce, especially in terms of bubble diameter, liquid volume fraction, and foam uniformity (meaning no initial gradients, holes, etc). Despite this till today exists a lack of general methodology for foam generation. Foam fraction are generated in various ways. The most familiar is simply to vigorously shake a closed container partially filled with surfactant solution. The other commonly used automatic foaming methods are: i) gas aeration in the foam column, where the gas is blowing by the porous membrane, ii) mechanical flipping, shaking or vibrating in various closed containers (i.e. in Hele-Shaw cell), iii) using various kind of mixing devices (homogenizers, turax, etc.) or iv) in special apparatus, via turbulent mixing of gas with a narrow jet of a surfactant solution inside a delivery tube. The cross-linking comparison of the methods validity is almost impossible. Let's short describe positive and negative points of those methods.

Foam in the column starts to form when the numbers of bubbles arriving to the solution surface exceed the number of rupturing bubbles [31]. The lifetime of the single bubble is determined by the composition of the solution (surface activity and concentration of the detergent) and by state of adsorption layers in the thin film in upper part of the bubble. Similar process of the gas dispersing into bubbles is hard to control because there are different interdependent interactions between the bubbles, which were formed under dynamic conditions and rising in chaotic stream under the buoyancy force. The bubbling method is slow, what leading the significant change of the liquid content along the foam height. The foam fraction is drier at top and wetter at bottom. Drainage may also cause the variations of the adsorption equilibrium coverages in the foam films. During similar dynamic measurements, the variation of the height of the foam and the solution level with the time were recorded. The foam power (foamability) is determined from the height of the foam just after the generation, while foam stability is described by measuring rate of foam volume decreasing (or/and solution recovery rate) with the time.

As it was already mentioned foam can be also created in some closed cells partially filled with the surfactant solutions, like Hele-Shaw cell, using special mechanisms such as flipping, shaking or vibrating [22, 32, 33]. Due to wetting on the cell walls, thin liquid films are created during each flip or shake cycle. Starting with a large bubble over a liquid pool, it is clearly shown that successive cycles lead to the formation of foam composed of many bubbles. This foam obeys statistical laws that are highly reproducible. Similar method is really good for characterising the foaming power and foam stability. Differentiation of the foaming agents could be there done using few, relative simple parameters, as an evolution ratio of the number of bubbles composing the foam and foam homogeneity (which can be expressed in terms of bubble size distribution or spatial organization).

From the rheology measurements point of view, both described above methods have one major disadvantage. Samples created in the foam column or in Hele-Shaw cell couldn't be removed from the "generator" and injected to the rheometer measuring geometry.

Mechanical homogenizers such as mixers (blenders, handheld homogenizers => rotor--stator or turax devices) work by shearing which is created by a tangential force being applied to the sample [34]. They can foaming large samples quickly and are easy to use. Laboratory blenders or rotor-stator devices are available in stainless steel which allows fast and easy decontamination or sterilization. Rotor-stators are designed with an outer stationary tube (stator) and an inner turning shaft (rotor) which is connected to a motor. At the bottom of the rotor-stator are slots on both the tube and shaft. When running at 5000–30000 rpm, samples pressed into the slots of the rotor-stator are efficiently sheared. However, what is important from our point of view, the high speed homogenization created heat and vortexes, which can cause a significant protein denaturation. Despite this similar devices are commonly used for the food foaming experiments [35–41].

To avoid the experimental problems describing above, a simple apparatus based on fire fighting technology have been constructed for reproducible foam generation [42]. The center of the apparatus is a cylindrical brass mixing chamber into which both gas and solution are metered at steady rate. To force surfactant solution into the chamber, the high pressure in a reservoir is raised by a bottle of compressed N_2. This produces a powerful jet of liquid through a tiny hole in the center of the chamber. To produce foam, gas is simply fed into the jet-side of the chamber. This method allows producing large volumes of uniform foam rapidly, with a liquid content that is easily varied.

5. Foam rheology – introduction

Foams rheology is a difficult subject due to the complexity of their structure and the nature of their components (gas, liquid, surfactants, surface-active biopolymers or particles) [2, 5–7, 11, 43–49]. Moreover, as others foam ageing processes, the rheology is also interdependent. The slow creep below the yield stress can caused the changing of foam structure and coarsening. Therefore it could be counted as a fourth dynamic process occurring in the foam fraction (after drainage, coarsening and collapse). Multiple factors influenced the rheology of foams, including: liquid bulk properties, gas properties, air phase volume, liquid volume fraction, solution viscosity, interfacial thin film visco-elasticity, bubble size distribution, and bubble shape. A nature of the adsorbed surfactant or biopolymer and state of adsorption layer also modified the properties of the thin liquid film which separate the bubbles.

As is generally known rheology give us information how the materials respond to applied forces and deformations. The rheological evaluation is basing on simple concepts of stress (force per area) and strain (deformation per length). Stress (σ) is always a measurement of force per unit of surface area and is expressed in units of Pascals (Pa). The storage moduli G' gives us information of the deformation energy stored in the sample during the shear process, describing the elasticity properties.

$$G = \phi_{gas}(\phi_{gas} - \phi_c)\frac{T}{r} \tag{1}$$

Where the ϕ_{gas}, ϕ_c, T and r are gas volume fraction, critical gas volume fraction, surface tension and bubble radius, respectively. Beyond the critical gas volume fraction the foam cells (spheres) come apart and the foam loses it mechanical stability and becomes a bubbly liquid. This loss of foam stability is also known as the rigidity loss transition point. In te case of aqueous foams the critical points is equal ca. 64% ($\phi_c = 0.64$).

The loss moduli G'', which present the viscous properties of the sample, shown deformation energy used to the shear and lost to the sample.

$$\sigma_{yield} = (\phi_{gas} - \phi_c)^2 \frac{T}{r} \tag{2}$$

When flow occurs in foam, the bubbles must slide past each other. If the stress is progressively increased, the structure yields and plastic flow sets in. During the deformation, when the bubbles are strained, the osmotic pressure is exerted and bubbles store surface energy. Hence, foams exhibit linear viscoelastic behaviour when they are subjected to small shear stresses while they flow like viscous liquids when the applied shear stress is large enough to trigger bubble rearrangements. This behaviour is related to the foam structure on the bubble scale. It therefore has a yield stress, and belongs to that category of complex materials that may be termed "Bingham fluids", with a viscosity inversely proportional to shear rate. The scale of the shear moduli as well as the yield stress in this situation is set by the Laplace pressure of the bubbles.

In the linear regime the static shear moduli is governed by well-known Princen law as a function of liquid fraction, average bubble size and surface tension [7, 42]. However, as it was already mentioned, foam is a dynamic and non-equilibrium system. In reality the truly static elastic behaviour hasn't existed there [48]. Even if drainage and bubble coalescence could be suppressed, the foam is ageing due to process of Oswald ripening. Upon a ripening induced rearrangement, the bubble packing locally settles into a new configuration of minimal energy, so that the elastic strain induced by the applied macroscopic stress is at least partly converted into an irreversible strain. The local elastic stress existing prior to the rearrangement is thus relaxed [2, 46, 47].

For strain beyond yield strain, packing of the bubbles undergoes irreversible topological changes and non-Newtonian liquid-like behaviour occur [2]. Yielding typically occurs at strains of the order of 0.1–1, sufficiently large so that nonlinear elastic behaviour may be expected before the onset of significant plastic flow. However, the passage between these two types of mechanical behaviour is not yet well understood. When an elastic material is subjected to shear strains that are large but insufficient to induce significant plastic flow or yielding, the induced shear stress is accompanied by unequal normal stresses. This nonlinear phenomenon, known as the Poynting effect [50, 51], is governed by a universal relation between shear strain and first normal stresses difference, valid for nondissipative isotropic elastic materials. It was experimentally shown that the similar effect exists also in aqueous foams [52]. The viscoelastic linear properties and yield stress are strongly dependent on the liquid fraction, and for a low molecular weight surfactant, providing "fluid-like" interfaces, a universal behavior was recovered [53].

It was also shown that transient relaxation region, between the initial elastic responses and finally a steady state foam flow exists [54]. The effect was explained as a consequence of intermittent temporary loss of elasticity upon coarsening-induced structural rearrangements on the bubble scale.

6. Foam rheology – experimental problems

The physical measurements of foam rheological properties are complicated by its inherently unstable nature, foam ageing and by the presence of a liquid film slip layer at the wall. Traditional rheometer geometries, such as parallel plates, cone-plate or Couette tend to experience wall slip and could cause foam structure destruction during sample loading. Till today no general and uniform methodology for foam rheology measurements were developed. Therefore the direct comparison of various experimental data is complicated and often impossible.

The liquid film layer generated at the flat wall could easy slip during the experiments, what affect the accuracy of measurement [55, 56]. Some techniques could be applied for the minimize wall slip, like:

i) an additional hydrophobization of the walls,
ii) sandblasting (roughening) of the flat stainless steel or acrylic geometries (cone or plate),
iii) covering of cone and plates by polydisperse sand grains,
iv) specially grooved, cross-hatched of serrated geometries or
v) vane tool. It is hard to qualify which geometry is the best for the foam rheology experiments.

However, few general marks could be pointed. Despite the geometry choose, the both measuring parts of the device (parallel plates, cone and plate, Couette cup and bob or the vane toll and cup) must be prepared to prevent foam slipping. Without it, the wall slip will happen on the flat or smooth surface and the experimental data will be unreliable.

The parallel plates (serrated, cross-hatched or covered by sand grains) are the most adequate experimental tool in the order to measure foam rheology. However plate-plate geometry has a limitation and is insufficient in the case of transient foams. In similar foams, where collapse of the foam reduces the sample height, the disengaging of the foam from the upper plate happens.

Some author suggests that the foam compression during the sample loading into plate-plate geometry, and connected with this some distortion of foam structure, could cause the rheological properties of the material [57]. However, together with the letter author own experiences basing on the experiments with Gillete foam cream [58], in the linear regime the results are independent of gap width (plate-plate => gap variation 2–5mm, cone-plate => gap 0.15 mm) and consistent for cone-plate and plate-plate geometries, excluding artifacts due to wall slip or finite size of the gap compared to bubble structures.

Yield stress of foams depends strongly on gas volume fraction, bubble radius and surface tension. Therefore it is important to characterize these foam parameters throughout the full duration of the experiment. Thus, the bubble size should be measured using some digital camera. Images will be there captured at certain time intervals during the foam drainage process to give details on how the bubble size changed with time during the experiments.

The gas volume fraction in the foam could be measure by various methods. However, almost none of them could be coupled with the rheological test in rheometer. The only "in situ" method is a study of the local structural rearrangements rate in ageing foam using diffusing-wave spectroscopy DWS. The samples should be there injected between the transparent glass plates of the rheometer [54].

The other method for gas volume fraction ϕ_{gas} verification is a simultaneously experiment in Hele-Shaw cell [32, 33]. The measurements is basing on the series of following snapsots of the foam fraction. On the foam pictures, the drainage effect can be monitored by measuring the light intensity transmitted through the bubble edges. In so doing, the liquid fraction φ that is actually measured on the Hele-Shaw walls slightly differs from the 'bulk' liquid fraction φ. Nevertheless, φ gives the relevant information about the liquid flows inside the bubble edges [22, 32, 33].

The air volume fraction could be also measured by the gravimetrically method [59]. A syringe with known volume is there filled with foam and weighed. The air volume fraction in the foam is determined from the relation $\phi_{gas} = 1 - m_F/(V_F\rho)$, where m_F is the mass of the foam in the syringe, V_F is the respective foam volume, and ρ is the mass density of the foaming solution.

The serious problem is connected with the water evaporation from the measured wet foams samples. It is clear that the evaporation is equal with the destruction of foam structure due to faster coarsening. To prevent the evaporation, the air in contact with the foam should be saturated. The samples should be therefore closed during the viscoelastic measurements in special, additional humidity cell. All the experiments must be carried out at constant temperature.

The coarsening of the foam could be suppressed by the using of hexafluoroethane C_2F_6, which has much lower diffusion and solubility constants then air or N_2 [49]. Similar effect could be done by mixing of nitrogen saturated with perfluorohexane vapor and special surfactant solution formulation [60].

7. Foam rheology – measurements methodology

The measurements of the foam rheological properties and for detecting the occurrence of nonlinearities and yielding could be done in various ways [2, 49–54]. Two types of oscillatory experiments can be performed: amplitude sweep at fixed frequency or frequency sweep at fixed amplitude. However, the foam ageing (drainage and coarsening) mostly do not allow low frequency experiments. So therefore in the case of wet foam the amplitude sweep measurements are used (oscillations at a fixed frequency $\omega = 1$ rad s^{-1} and with a strain amplitude γ varied from 10^{-4} to 1). It allow to measure storage and loss moduli (G' and G''), and to determine linear and non-linear responses (yielding) of foam fraction. The creep experiments could also be performed, where the foam is subjected to a constant stress Σ. In such experiment the resulting strain γ and compliance J ($J = \gamma/\Sigma$) [2, 42, 61] are measured versus time.

Fig. 3 and 4 present a typical result of strain-sweeps for shaving foam at a fixed liquid volume fraction. This sweep procedure consists in the application of a strain g varying from 0.001 up to 10, at a constant frequency of 1 Hz. The storage G' and the loss G'' moduli are classically obtained from those measurements. For all wet foams, the amplitude sweep curves keep the same classical shape with only variations for the plateau values G_0.

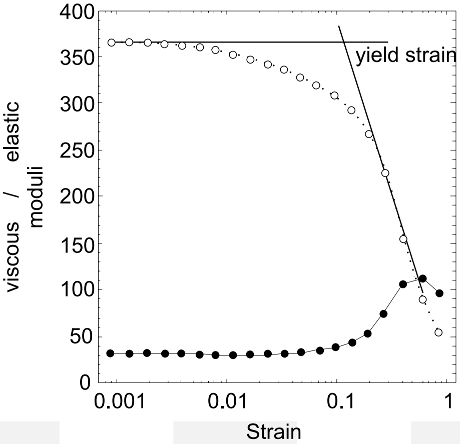

Fig. 3. (left) Evolution of the elastic and loss moduli with the applied stress amplitude. The intersection presents the foam yield strain. (Measurement was done by Bohlin Gemini II rheometer, equipped with serrated parallel plates, 4 mm gap)

Rys. 3. (po lewej) Zmiany modułów zachowawczego i stratnego w funkcji amplitudy naprężenia. Punkt przecięcia prostych prezentuje granicę plastyczności w funkcji naprężenia. (Eksperymenty wykonane przy pomocy reometru Bohlin Gemini II, wyposażonego w układ podwójnych, nacinanych płytek, odstęp między płytkami 4 mm)

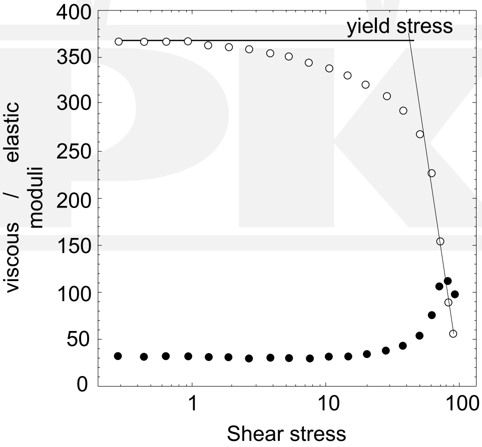

Fig. 4. (right) Evolution of the elastic and loss moduli with the applied strain amplitude for Nivea shaving cream. The intersection presents the foam yield strain

Rys. 4. (po prawej) Zmiany modułów zachowawczego i stratnego w funkcji amplitudy ścinania – dla pianki do golenia Nivea. Punkt przecięcia prostych prezentuje granicę plastyczności w funkcji ścinania

Yield strain and yield stress also could be determined from oscillatory data. A possibility consists in representing G' versus stress amplitude σ (or strain amplitude γ) in a log–log plot (Fig. 3). The behavior well above and well below the yield stress is well described by power laws corresponding to straight lines in such a plot. Their intersection provides an empirical definition of a yield stress σ_y. It can be used the parallel analysis to determine the yield strain γ_y using a log–log plot of G' versus strain amplitude γ (Fig. 4).

8. Foam rheology – surfactants and proteins foams

The liquid foam rheology has been studied extensively during last twenty years. However it can be easy noticed, that the numbers of surfactant foams systems (solutions and foams compositions) described by reliable rheological experiments are a very limited. The surfactant or polymer foams described below were formed mostly under high pressure is some variations of turbulent mixing devices [42].

Khan et al. used the polymer-surfactant aqueous solution as a foaming liquid [62] (parallel plate geometry with discs covered by the sandy paper). Politova et al. present the effect of two commercial cationic polymers (Jaguar C13c and Merquat 100) on the foam rheological properties (also using parallel plate geometry covered by the sandy paper) [59].

Cohen-Addad et al. [48, 54, 58, 63], Höhler et al; [64], Krishan et al. [65], Rouyer et al. [60, 66] and Labiausse et al. [67, 68] studied extensively the foam stability and rheological properties in various surfactant based systems, like:

i) Gillette shaving cream [48, 54, 60, 63–65],
ii) tetradecyltrimethylammonium bromide TTAB [60] (TTAB 0.936%, g/g, dodecanol 6.24×10^{-4}%, g/g and glycerol 50%, g/g),
iii) sodium dodecyl sulfate SDS [66] (SDS, polyethylene oxide PEO, dodecanol, and butanol),
iv) polymer-surfactants [48, 67, 68] based aqueous solution contained sodium α-olefin sulfonate AOK, polyethylene-oxide and dodecanol (concentrations: $1{:}5\%$ g = g, $0{:}4\%$ g = g, and $0{:}2\%$ g = g, respectively),
v) Sodium Lauryl-dioxyethylene Sulfate SLES [65, 69] (SLES 0.33% g/g, Cocoamidopropyl 0.17% g/g and Glycerol 99.5%).

The Couette grooved geometry, grooved cone – serrated plate or serrated parallel plates were used in mentioned experiments. The rigidity of the particle-laden Gillette foams was also evaluated (grooved cone-serrated plate tools) [58].

Saint-James and coworkers [70] present the rheological study of foam generated from a mixture of surfactants α-olefin sulfonate AOS, polyacrylic acid polymer CARBOPOL 941, and cosurfactants dodecanol in solvent mixture butanol/water (two different measurement devices were used,

i) Couette cell, where the walls of both cylinders have been covered with sand paper,
ii) sandblasted cone-plate device made of transparent acrylic).

The influence of the doped colloidal Laponite on the SDS foam stability and rheology were measured in the same geometrical system [71]. Recently, Salonen et al. [72] provide the data describing the rheology of foams generated basing on cationic ammonium bromide surfactants;

i) monomers dodecylTAB (DTAB),
ii) tetradedylTAB (TTAB) and
iii) oligomers of DTAB with the degree of polymerization x varied from 2 to 4 and the spacer length s equal to 3 or 6 (plate-plate configuration with the gap was 2 or 3 mm).

In the case of biopolymer based foams the literature of subject is even more limited. Only the rheology of foams generated from various egg, white egg or whey proteins were studied using the vane tool or serrated parallel plate geometries. However, all described below tests were performed on the foam samples generated by various mixing devices with different methodology.

The Pernell with co-workers measured the yield stress of foams based on egg white and whey protein isolate (homemade vane tool) [57, 73]. Luck et al. [37] and Davies et al. [38, 39] described the factors determining yield stress in the whey protein foams (vane geometry). Mleko with coworkers [35] measured the rheological properties of foams based on egg albumin after pH treatment using cross-hatched parallel plates. The same geometry was used by Nastaj and Mleko [36] and Nastaj [40] during evaluation of calcium chloride concentrations [36] or pH effects [40] on rheological properties and stability of foams obtained from different whey protein propagates.

Together with the best knowledge of the author letter in the whole literature of subject exist only one set of experiments, where the rheological properties of surfactant (SDS) and protein (casein) foams were compared in well defined and controlled conditions. Marze and his coworkers [49, 74, 75] carefully studied the influence of:
i) surfactant solution composition,
ii) gas volume fraction,
iii) bubble size,
iv) foam age,
v) bulk viscosity,
vi) gas diffusion rate and,
vii) wall slip conditions – on the foam stability and rheology properties.

The foams were produced by using a turbulent mixer apparatus [42], which was mentioned above in the section “foam generation”. The foam liquid volume fraction, controlled by adjusting the gas and liquid flow rates in the foam generator, was varied from 0.05 up to 0.25. For the gas, the use of nitrogen N_2 and perfluoroethane C_2F_6 allowed to control the rate of coarsening and drainage of the foams. The three types of foaming chemicals were used;
i) sodium dodecyl sulfate SDS, an anionic surfactant;
ii) casein CAS, a mixture of milk proteins; and
iii) Amilite GCK-12 GCK, a commercial name for an anionic surfactant made of a fatty acid residue from coconut oil.

The rheological parameters of the foams were studied using the homemade cone-plate geometries in transparent Plexiglass coupled with transmission diffusing wave spectroscopy (DWS).

It was shown that the normalised storage moduli $G_0/(\sigma/R)$ turns out to be almost constant and independent of the chemicals used [49] at 85% gas volume fraction. No big differences were found between protein (casein) and surfactant (SDS) foams, what is in opposition to results for emulsions. The main reason for this was probably too high surface tensions always present in foams. Surface tension is always much bigger than any interfacial elasticities. In contrary authors observed the huge differences in the behaviours of the loss moduli G_0'''', which was about 4–5 times higher for the casein foams than for the SDS ones. It could be estimated that some extra dissipation occurs in the casein foam due to the solution viscosity or/and from the thick structure and texture of protein lamellae foam film.

The influence of the solution bulk viscosity on the foam properties is still not clear. Some authors claims that the increasing of the bulk viscosity improved the foam stability [27]. While the others [49] shown that with 300% increasing of the bulk viscosity caused only minor variations of the storage and loss moduli. It suggests that the foam linear viscoelastic properties are almost independent from the bulk viscosity [49].

It was also proved that the foam viscoelastic linear properties and yield stress were strongly dependent on the liquid fraction. The storage and loss moduli and yield stress values decreases with the gas volume fraction decreasing (5–30%) [75]. Foam becomes less elastic as the liquid fraction increases, since the bubbles are less and less packed. For low molecular weight surfactant foams, which have the "fluid-like" interfaces, and universal behavior was recovered. In the case of protein foams the discrepancies was connected with interface and thin film properties.

The variations of the storage and loss moduli with the foam age were clearly described as a result of foam drainage and coalescence [49, 74, 75]. The ageing evolution of the foam was changed by the selection of the gas with the proper diffusion and solubility conditions (C_2F_6). Thanks for it the foam almost no coarsening occur and foam age only due to the drainage process. In the result the bubbles get more packed with the foam age and the storage (elastic) moduli is increasing with the time. In opposite cases, where the coarsening dominates over the drainage, the storage moduli is decrease with the time. The crucial role of coarsening in the long time liquid foam ageing was also confirmed [49].

9. Concluding remarks

Foam rheology is still a quite new area of scientific research. The numbers of various foams systems (different surfactants or biosurfactants solutions and/or foams compositions), which are described by proper viscoelastic experiments, are still relatively limited. Many of existing measurements are valid only under the experimental conditions described by the authors. The various methods of foam generation and the different rheological examination methodology lead the additional problems. The foam samples were studied by cone-plates, parallel plates (with various gap width), Couette cups, vane tools and others geometries Therefore the analysis and comparison of the data are really complicated. Some additional experimental errors, caused by the foam ageing, wall slip or other sources have also the strong influence on the obtained data.

It must be say, that there have been many important advances in the field of aqueous foams rheology during recent years. It was clearly shown that the foam stability and its rheological properties are controlled by various parameters, like:

i) the conditions of the surface layer that protect the air-water lamellae interfaces,
ii) surfactant solution composition,

iii) gas volume fraction,
iv) bubble size,
v) foam age,
vi) gas diffusion rate and,
vii) wall slip conditions.

However, the additional tests with other foams systems under other conditions (new chemical compositions and other foams parameters) should be done. Without it the further progress in the investigation of foam behavior seems to be impossible.

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