Journal of Food Engineering 146 (2015) 53–61

Contents lists available at ScienceDirect

Journal of Food Engineering

journal homepage: www.elsevier.com/locate/jfoodeng

A geometrical interpretation of large amplitude oscillatory shear (LAOS) in application to fresh food foams

Paweł Ptaszek *

Agriculture University in Krakow, Faculty of Food Technology, Department of Engineering and Machinery for Food Industry, ul. Balicka 122, 30-149 Kraków, Poland

ARTICLE INFO

Article history:
Received 16 April 2014
Received in revised form 7 August 2014
Accepted 27 August 2014
Available online 10 September 2014

Keywords:
Foam
Large amplitude oscillatory shear (LAOS)
Chebyshev transform
Protein
Hydrocolloids
Lissajous pattern

ABSTRACT

In this research, we studied the rheological properties of wet food foams, consisting of egg white protein, inulin and xanthan gum. The rheological analysis was carried out using the large amplitude oscillatory shear (LAOS) technique. For the obtained results, we constructed two types of Lissajous figures in deformation/stress and shear rate/stress coordinate systems. A geometrical decomposition of the obtained figures was performed, which allowed the isolation of stress values for nonlinear pure elastic and pure viscous properties accordingly. With the use of the Fast Chebyshev Transformation (FCT) analysis, we were able to obtain the values of the Chebyshev coefficients. The knowledge of the elastic and viscous Chebyshev coefficients allowed for the interpretation, with high resolution, of nonlinear rheological properties of the obtained foams. It was found that supplementation with inulin stabilizes the structure of a foam based on egg white protein only. Supplementation with xanthan gum, however, increases the tendency towards flow.

1. Introduction

Foams in food are one of the most often-occurring dispersion systems (Campbell and Mougeot, 1999; Miyazaki et al., 2006; Balerin et al., 2007). Thermodynamically, foam is a metastable system (Sollich et al., 1997; Sollich, 1998) with a natural tendency towards disintegration into liquid and gas phases. This phenomenon can be prevented by the usage of appropriate additives, which can be divided into two groups. The first comprises substances forming a suitable layer at the liquid–gas interface and thereby preventing the coalescence of gas bubbles (Prins, 1988; Marze et al., 2009). The second group comprises polysaccharides, which increase the viscosity of the continuous phase and significantly limit the gas bubbles' mobility; hence, they inhibit the bubble aggregation and prevent the degradation of the foam (Prins, 1988; Balerin et al., 2007).

One of the most frequently used polysaccharides in the food industry is Xanthan gum (Morris, 2006; Palaniraj and Jayaraman, 2011). Recently, inulin has also become quite popular, due to its application possibilities (Franck, 2006). Inulin is a polysaccharide (oligosaccharide) of plant origin, mostly extracted from bulbs, rootstocks and roots of chicory, Jerusalem artichoke and dahlia (Franck, 2006).

The rheological properties of foams stabilized with polysaccharides are quite diverse; they exhibit a wide spectrum of behaviors ranging from simple Newtonian viscosity to elastoviscoplastic phenomena (Rouyer et al., 2005; Ptaszek, 2013; Żmudziński et al., 2014). The use of polysaccharides as foam-stabilizing factors allows for flexible shaping of the foam's mechanical properties. This is particularly applicable for fresh wet foams, which are subject to further processing, such as pumping or forming into adequate shapes. All of these technological processes are based on subjecting the foam to shear flow.

Most processes occurring during the flow of food are of nonlinear nature. For fluids not exhibiting any elastic properties, the nonlinearities can be characterized as deviations from the Newton's rule. Simple deviations can be described by Ostwald-de Waele type equations ($\tau = k\dot{\gamma}^n$). More complex deviations are typical for food fluids, whose viscosity depends on the shear rate and shear time values. In this case, the specification of rheological properties requires application of one of the structural theories, as well as a specific fluid state equation (Ptaszek, 2012). A separate group of food systems comprises viscoelastic systems, such as biopolymer solutions, dough, and starch pastes, which can be in either a liquid or solid form. Thus far the research on these systems has been conducted predominantly within the linear viscoelasticity range. The results of these studies provide information on relaxation or retardation phenomena occurring in the studied materials (Ferry, 1980). There are predominantly two types of experiments carried out, either within the time or the frequency domain. For the frequency

* Tel.: +48 126624768; fax: +48 126624761.
E-mail address: p.ptaszek@ur.krakow.pl

http://dx.doi.org/10.1016/j.jfoodeng.2014.08.022
0260-8774/

domain, two types of experiments are conducted: the function of the strain amplitude (γ) or stress (τ) (at constant frequency), or the function of frequency (at constant strain amplitude or stress amplitude). Recently there is much interest in research methods that expand the possibilities of classical studies within the frequency domain. These methods are called large amplitude oscillatory shear (LAOS) and Fourier Transform Rheology (FTR) (Hyun et al., 2011) and both subject the material to cyclic deformations (sinusoidally variable in time) with suitably high amplitude (γ_0):

$$\gamma(t) = \gamma_0 \sin(\omega t) \tag{1}$$

In nonlinear conditions, the material's response can be estimated with high accuracy by utilizing the following harmonic function:

$$\tau(t;\omega,\gamma_0) = \gamma_0 \cdot \sum_{n:odd} [G'_n(\omega,\gamma_0)\cdot \sin(n\omega t) + G''_n(\omega,\gamma_0)\cdot \cos(n\omega t)] \tag{2}$$

In the case of small strains there is only one harmonic present and, hence, G'_1 and G''_1 become real (G') and imaginary (G'') parts of the complex dynamic modulus ($G^* = G' + iG''$), well known from studies of linear viscoelasticity.

The analysis of the obtained function Eq. (2) requires the use of extended harmonic analysis based on Fourier transform, as well as a description utilizing the phase plane (analysis of Lissajous figures) (Hyun et al., 2011). As a result, new rheological parameters are obtained, describing the material's behavior within the nonlinear range of deformations or stress. These parameters can be strictly interpreted physically and allow the prediction of the rheological properties of the studied materials, hence facilitating the creation of new food products and industrial plants. Broadly defined mechanical properties of food, within the nonlinear area, also play an important role in modeling the behavior of the product during consumption in the oral cavity.

The analysis based on 3D Lissajous figures (Ewoldt and Mckinley, 2010) deserves particular attention. Such figures are built within a 3D coordinate system of strain/shear rate/stress. The curve in shear rate–stress plain can be obtained by differentiating the forcing function (Eq. (1)). It means that the analysis of 3D Lissajous figures requires the recording of the forcing function (strain) and the response of the material. The obtained closed curve represents both elastic and viscous properties of the studied system. This figure can be split into two figures in 2D coordinates (Fig. 1a): deformation/stress and shear rate/stress. Whereas the first figure describes the elastic properties of the system, the second figure describes its viscous properties. The described procedure for dividing into two Lissajous figures stems from the lack of possibility to easily differentiate the resulting signal into parts, that would describe either purely the elastic behavior or the viscous behavior. It is impossible to clearly distinguish the factors describing the storage of mechanical energy (G') and the dissipation of the energy (G''), as is the case when applying the small amplitude oscillatory shear (SAOS) technique. This is due to the fact that the response of the material (Eq. (2)) contains higher harmonics responsible for the nonlinear character of the material.

A direct application of FTR methods merely allows determining the degree of nonlinearity in the material's response; it does not allow one to consider the overall impact of elastic and viscous parts on the evaluation of the observed rheological occurrences (Klein et al., 2007; Hyun and Wilhelm, 2009). Moreover, FTR methods allow the reconstruction of a time series using individual harmonics and their phases (Hyun et al., 2011). The reconstructed time series is free of noise; therefore FTR can be used as a highly effective filtration method for experiments containing noise levels.

One of the possible methods, which can be applied in the analysis of the above cases, is the geometrical decomposition of the 2D Lissajous figures presented by Cho et al. (2005). According to the method's premise, stress (τ) can be subjected to decomposition as expressed by the equation:

$$\tau(x,y) = \frac{\tau(x,y) - \tau(-x,y)}{2} + \frac{\tau(x,y) - \tau(x,-y)}{2} = \tau'(x) + \tau''(y), \tag{3}$$

where $x = \gamma$, $y = \dot{\gamma}/\omega$; the $\tau'(x;\gamma_0,\omega)$ value stands for elastic stress, and the $\tau''(y;\gamma_0,\omega)$ value corresponds to viscous stress. This procedure can be summarized as the division of the Lissajous figure into four parts: $\tau(x,y)$, $\tau(x,-y)$ and $\tau(-x,-y)$, $\tau(x,-y)$. The dividing operation is possible only when the figure is closed. The values τ' *and* $\tau''$are arrived at by subtracting appropriate parts of the Lissajous figure, according to the Eq. (3) (the lack of $\tau(-x,-y)$ is due to the symmetry conditions $\tau(-x,-y) = \tau(x,y)$).

This results in two curves, as presented in Fig. 1a. The curves divide the Lissajous figure into two parts of equal area. The advantage of this approach is a decomposition of the resulting nonlinear signal into parts corresponding to the elastic and viscous properties, without the necessity to apply any constitutive equations (Cho et al., 2005).

The curves may be subjected to further decomposition. There are two methods usually used for this: the first applies regression analysis and the method of least squares (Cho et al., 2005), whereas the second procedure is based on Chebyshev polynomials of the first kind (Ewoldt et al., 2008), obtained according to the recurrence rule:

$$\begin{aligned} T_0(x) &= 1 \\ T_1(x) &= x \\ T_n(x) &= 2x\cdot T_{n-1}(x) - T_{n-2}(x) \end{aligned} \tag{4}$$

Then $\tau'$and τ'' can be expressed by the following relations:

$$\begin{aligned} \tau'(\bar{x}) &= \gamma_0 \sum_{n:odd} e_n(\omega,\gamma_0)\cdot T_n(\bar{x}) \\ \tau''(\bar{y}) &= \dot{\gamma}_0 \sum_{n:odd} v_n(\omega,\gamma_0)\cdot T_n(\bar{y}) \end{aligned}, \tag{5}$$

where $\bar{x} = x/\gamma_0 = \gamma/\gamma_0, \bar{y} = y/\gamma_0 = \dot{\gamma}/\dot{\gamma}_0$; the scaling is a result of the orthogonal conditions of the Chebyshev polynomials (Boyd, 2001). The coefficients e_n and v_n are called Chebyshev weighting coefficients and they represent the elastic and viscous parts in the nonlinear viscoelasticity, respectively. The distribution of the e_n and v_n coefficients' values is depicted in Fig. 1. It should be noted that the Fourier coefficients (G'_n, G''_n) in Eq. (2) fully characterize the response of the material in the time domain; however, the physical interpretation of the higher harmonics may only be carried out based on the e_n and v_n Chebyshev coefficients (Ewoldt et al., 2008; Hyun et al., 2011).

The Chebyshev coefficients can exhibit both positive and negative values (Hyun et al., 2011). The e_3 and v_3 values are a time-independent measure of the material's nonlinearity against its elastic and viscous properties. The higher order Chebyshev coefficients (n = 5, 7, ...) can also be interpreted as a measure on the material's nonlinear response. The third coefficients, e_3 and v_3, are predominantly analyzed as the main parameters of nonlinearity.

Typically, the interpretation of the liquid's properties is carried out by determining the values of e_3 and v_3:

$$e_3 = \begin{cases} > 0 & \text{strain-stiffening} \\ = 0 & \text{linear elastic} \\ < 0 & \text{strain-softening} \end{cases} \quad v_3 = \begin{cases} > 0 & \text{shear-thickening} \\ = 0 & \text{linear viscous (Newtonian)} \\ < 0 & \text{shear-thinning} \end{cases} \tag{6}$$