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Non-linear rheological behavior of water in water emulsions

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Abstract

We studied the large amplitude oscillatory shear (LAOS) behavior of water-in-water (W/W) emulsions stabilized by 0.25 wt% basil seed gum (BSG) + 0.5, 1, 2 wt% waxy corn starch (WCS) and 0.2 wt% BSG + 0.5, 1, 2 wt% high pressure treated waxy corn starch (HWCS). At each BSG level, increasing concentrations of WCS and HWCS resulted in a notable decrease in nonlinearity, while the shear thickening factors and strain stiffening values increased. Additionally, the values of G''_3/G''_1 were significantly lower than those of G'_3/G'_1.

Keywords: *Lissajous* plot- Non-linear viscoelastic- Rheology- Water in water emulsion

Introduction

The W/W emulsions are created from a binary polymeric system that uses biocompatible ingredients like proteins and polysaccharides, making them a safe and effective option for use [1]. Basil seed gum (BSG) is a new, all-natural emulsifier used in food preparation [2]. Waxy corn starch (WCS) is a widely used food ingredient used as a thickener, stabilizer, and gelling agent. The high hydrostatic pressure (HHP) process alters the functional qualities of starch sources [3]. Rheological effects have a role in W/W emulsion storage stability. According to Anvari and Joyner [4], the examination of large amplitude oscillatory shear (LAOS) characteristics in different food products is highly significant as it offers valuable insights into the micro- and macro-structural features of foods when subjected to large deformations. Our research led us to the conclusion that 0.25 wt% BSG+ 0.5, 1, or 2 wt% WCS and 0.2 wt% BSG+ 0.5, 1, or 2 wt% HWCS emulsions were stable W/W emulsions for at least a week [5]. In this study LAOS rheology of stable W/W emulsions (0.25 wt% BSG+ 0.5, 1, or 2 wt% WCS and 0.2 wt% BSG+ 0.5, 1, or 2 wt% HWCS) were investigated.

Experimental

Basil seed gum extraction

Based on the study conducted by Razavi et al. [6].

High hydrostatic pressure treatment of waxy corn starch (HWCS)

According to the research conducted by Heydari and Razavi [3].

Preparation of the W/W emulsion

Based on the study conducted by Zamani and Razavi [5].

Large amplitude oscillatory shear (LAOS) measurements

The non-linear (n-LVE) elastic and viscous properties of the emulsions were evaluated by conducting an amplitude sweep from 0.01% to 1000% at a constant frequency of 1 Hz and temperature of 25°C. The elastic Lissajous plots, the Fourier transformed examination in the time domain, and the strain stiffening feature (S factor) and shear-thickening property (T factor) within each cycle were determined according to the methodology proposed by Ewoldt et al [7] as follows:

$$S = \frac{G'_L - G'_M}{G'_L} \quad (1)$$

$$T = \frac{\eta'_L - \eta'_M}{\eta'_L} \quad (2)$$

Statistical analysis

The data was analyzed using SPSS, Duncan Multiple Range Test with significance levels set at p<0.05. The rheological data were fitted using MATLAB (2013a) software's Levenberg-Marquardt technique and curve fitting toolbox.

Results and discussion

LAOS characteristics

The elastic Lissajous-Bowditch plots of the W/W emulsions at 1000% strain and 1 Hz frequency are shown in Fig. 1. The limited elastic Lissajous plots decrease when WCS and HWCS concentrations increase from 0.5 wt% to 2 wt%, indicating greater

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resilience to disruption, more elastic-dominant characteristics, stronger stiffness, and lower energy dissipation. Samples containing HWCS had lower elastic Lissajous plots due to steric stability and smaller droplet size of HHP-treated starches. In addition to visual representation, it is important to employ measurable techniques to thoroughly investigate nonlinear shear stress responses. The W/W emulsions exhibited linear viscoelastic behavior when the ratio of G'_3/G'_1 and $G''_3/G''_1$was less than 0.01, which fell in the strains less than 10%. This was further supported by the Lissajous-Bowditch plots, which indicated perfect viscoelastic characteristics (data not shown). For all W/W emulsions at a 1000% strain, the amounts of these ratios were higher than 0.01, illustrating the nonlinear viscoelastic characteristic of the created emulsions (Table 1). In addition, the amounts of G'_3/G'_1 of the W/W emulsions were noticeably greater than the amounts of G''_3/G''_1, indicating the predominance of nonlinear elastic behavior in the W/W emulsions. Furthermore, the extent of nonlinearity decreased as the concentration of WCS and HWCS increased ($P < 0.05$). High concentrations and smaller droplet sizes of starches contribute to steric stability in W/W emulsions, resulting an efficient structure resistant to large strains. All W/W emulsions showed strain-stiffening and shear-thinning characteristics. Higher concentrations of HWCS in emulsions increased T parameter values, indicating stiffening. Higher S factor values indicated greater resilience and consistency under higher strains, possibly due to increased stiffness and structural stability.

Conclusions

We examined the behavior of W/W emulsions (comprising 0.2 wt.% BSG + 0.5, 1, 2 wt.% HWCS, and 0.25 wt.% BSG + 0.5, 1, 2 . wt.% WCS) under LAOS rheology conditions. By increasing the concentrations of WCS or HWCS at each BSG level, the degree of nonlinearity, exhibited a notable decrease. In contrast, the values of strain stiffening and shear thickening factors showed an increase.

References

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Table 1. The ratio of the third harmonic elastic modulus to the first harmonic elastic modulus (G'_3/G'_1) and the ratio of the third harmonic loss modulus to the first harmonic loss modulus (G''_3/G''_1), and strain-softening (S-factor) and shear-thinning (T-factor) parameters for the W/W emulsions

Samples	G'_3/G'_1	G''_3/G''_1	S	*T*
0.25BSG +0.5WCS	**0.451± 0.011[a]**	**0.091±0.010[a]**	**0.378± 0.054[f]**	**-0.195±0.032[d]**
0.25BSG +1WCS	**0.391± 0.024[ab]**	**0.074±0.021[b]**	**0.452± 0.068[d]**	**-0.157±0.025[c]**
0.25BSG +2WCS	**0.33±0.014[b]**	**0.052±0.011[d]**	**0.534± 0.088[c]**	**-0.135±0.014[b]**
0.2BSG+ 0.5HWCS	**0.201± 0.081[c]**	**0.062±0.001[c]**	**0.402± 0.096[e]**	**-0.179±0.078[d]**
0.2BSG+ 1HWCS	**0.159± 0.027[cd]**	**0.051±0.002[d]**	**0.625± 0.038[b]**	**-0.144±0.041[bc]**
0.2BSG+ 2HWCS	**0.110± 0.031[d]**	**0.043±0.001[e]**	**0.801± 0.095[a]**	**-0.110±0.031[a]**

A–f: Means followed by the same letters in the same column are not significantly different ($p > 0.05$)
BSG, basil seed gum, WCS, waxy corn starch, HWCS, high pressure-treated waxy corn starch

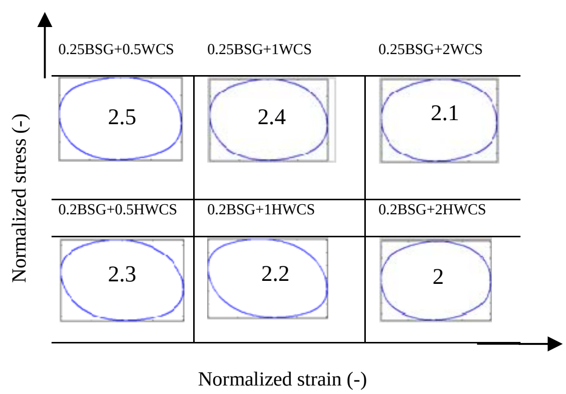

Fig 1. Elastic Lissajous-Bowditch plots of the W/W emulsions made by BSG and WCS or HWCS at a fixed frequency of 1 Hz, 1000% strain amplitude and 25 °C.