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Impact of emulsifier-polysaccharide interactions on the stability and rheology of stabilised oil-in-water emulsions

Kyriaki G. Zinoviadou[a], Thomas Moschakis[a], Vassilios Kiosseoglou[b], Costas G. Biliaderis[a] *

[a]*Department of Food Science and Technology, School of Agriculture*
Aristotle University of Thessaloniki, GR-54124, Thessaloniki, Greece
[b]*Laboratory of Food Chemistry and Technology, Department of Chemistry*
Aristotle University of Thessaloniki, GR-54124, Thessaloniki, Greece

Abstract

In the present study, the interactions between negatively charged sodium stearoyl 2-lactylate (SSL) and positively charged chitosan were studied in solution and on oil-water interfaces. Phase diagrams of the SSL/chitosan systems were obtained at both pH 4.0 and 5.7 by preparing concentrated solutions and mixing them at different ratios. Optical microscopy revealed that the complexes formed at pH=4.0 were smaller than those formed at pH=5.7 and that the size of the complexes decreased as the SSL/chitosan ratio was reduced. Emulsions (10% w/w oil) were prepared at pH=5.7 by using the complexes of a constant SSL concentration (0.4% w/w) and at different SSL/chitosan weight ratios. The droplet size of the emulsions that were formed with the complexes was greater than those containing only SSL. Using complexes of low SSL/chitosan ratio as emulsifying agent resulted in the production of emulsions with enhanced viscosity as determined by steady shear rheometry. However, none of the samples showed a gel-like behaviour since in all cases the G' (storage modulus) was lower that G'' (loss modulus). The presence of polysaccharide at the interface resulted in an increased stability of the emulsions subjected to environmental stresses, such as heat treatment and a freeze thawing process.

Keywords: chitosan; interfacial properties; complexes; emulsions; SSL

1. Introduction

Oil-in-water emulsions are widely used in the food industry and are produced by homogenization of oil and aqueous phases together. In order to stabilize emulsions emulsifiers are generally required. An

* Corresponding author. Tel. & Fax: +30-2310-991797
E-mail address: biliader@agro.auth.gr

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effective emulsifier should adsorb at the interface of the oil droplets, it should increase the surface pressure and should protect the droplets towards coalescence when the emulsion is exposed to environmental stresses [1]. Low molecular weight emulsifiers are highly effective in generating small droplets during homogenization but they provide low protection to destabilization processes. However, oil droplets with thicker interfaces can be created by using complexes of low molecular weight surface active components with non-surface active polysaccharides. These complexes are usually created by electrostatic interactions. Chitosan is a cationic polysaccharide whose charge characteristics are determined by its amino side groups. It has a rather extended conformation in solution and is widely used in food and pharmaceutical industries due to its biodegradability, biocompatibility and antimicrobial activity [2]. At relative low pH (<6.3) the chitosan chains carry a positive charge and the macromolecules remain soluble; however, as the pH of the solution increases, the chitosan loses its solubility due to deprotonation of the amino groups. Sodium stearoyl 2-lactylate (SSL) is an anionic surfactant manufactured by reacting stearic acid with food grade lactic acid in the presence of sodium. It is widely used in the food industry as improver (softener) in bakery products and in cream liquers [4].

Up to now, a large number of studies have been conducted on the use of opposite charged biopolymers to form the second and higher level layers around lipid droplets by electrostatic deposition [5]. However, little is known about the use of preformed emulsifier-polysaccharide complexes to stabilize oil-in-water emulsions [2, 6]. The aim of the present study was to investigate the interactions of SSL and chitosan in the bulk phase and examine the effect of pH on complex formation. Additionally, the ability of the complexes to stabilize oil-in-water emulsions was assessed and the stability of the emulsions under different environmental stresses encountered during food processing and storage was examined.

2. Materials & Methods

For experiments conducted at pH=4.0, a sodium acetate buffer (20mM) was used, while for those conducted at pH=5.7, a phosphate buffer (20mM) was employed. Aqueous stock solutions of chitosan (1% w/w) were prepared by dispersing chitosan into an acetic acid solution (pH=3.0) under gentle stirring and once the polymer was dissolved the pH was adjusted with NaOH solution to the desired value (4.0 or 5.7). SSL solutions were prepared by dissolving the emulsifier powder into the appropriate buffer solution overnight. For the construction of the phase diagrams different ratios of SSL to chitosan, at different total concentrations, were prepared by slowly adding the appropriate amount of the SSL stock solution into the chitosan-buffer solution under stirring. Oil-in-water emulsions at pH=5.7 were prepared by mixing appropriate quantities of the various SSL/chitosan complexes (SSL 0.4%, chitosan 0-0.48%), phosphate buffer and corn oil using an ultrasonic homogenizer (Sonics & Materials, Inc. Danbury, Connecticut, USA, Power 50/60Hz) for 2min, operated at 20s intervals. Optical micrographs of the complexes-stabilised emulsions were captured, after being diluted 10 times, by an Olympus BX 51 optical microscope fitted with a digital camera (Olympus, DP 50). Rheological measurements of the emulsions were performed by a rotational Physica MCR 300 rheometer (Phyica Messtechnik GmbH, Stuggart, Germany) using a concentric cylinder geometry in a controlled shear-stress mode. The temperature was regulated by a Paar Physica circulating bath and a controlled peltier heating system. To minimise dehydration, a solvent trap was employed. Small deformation oscillatory measurements for evaluation of the viscoelastic properties were performed at 20°C over the frequency range 0.1-100 Hz, at a constant deformation γ=0.1%. Flow curves were obtained and the controlled stress was varied in the range of 0.01-15 Pa. All rheological measurements were completed before any visual phase separation in the emulsion took place. The influence of various kinds of environmental stresses on the microstructure and the stability of the emulsions were evaluated. The freeze-thaw cycling stability was assessed by freezing the emulsion samples (-23°C for 24h) in plastic tubes and then thawing at 25°C for 3h. For the thermal processing, emulsion samples were transferred into glass vials that were stored in a water bath at 90°C for 30min.

3. Results & Discussion

State diagrams were constructed for the SSL/chitosan mixtures at different SSL concentrations (0.1-0.5%w/w) and varying weight ratios of the two components (0.8-5), at two pH levels (4.0 and 5.7). In all cases two different phases were observed: a cloudy upper layer dispersion and a transparent lower layer. The upper phase consisted of the insoluble SSL/chitosan complexes and its height increased with an increase of the total solids. The size of the complexes was estimated by optical microscopy (data not shown) and it was revealed that for all mixing ratios the size of the aggregates was bigger at pH 5.7 than pH 4.0. Previous studies on the mean particle size of aqueous dispersions of chitosan alone have shown that the mean particle diameter was relatively small from pH 3.0 to 6.0, and larger diameters were observed at even higher pH values, presumably due to decreased electrostatic repulsion, leading to insoluble aggregate formation [3].

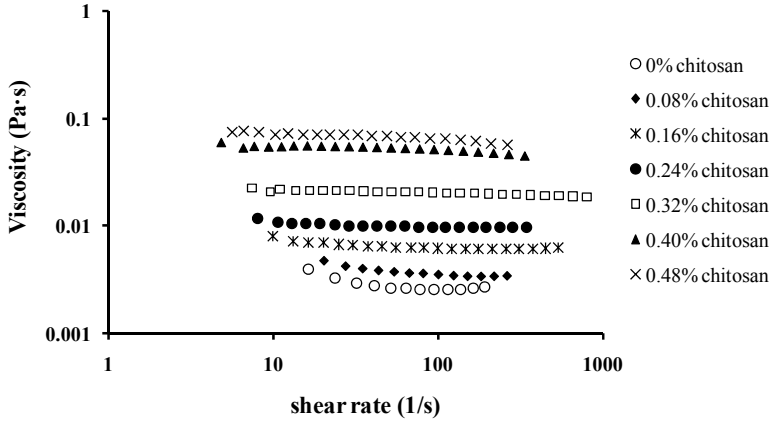

Fig. 1. Shear rate dependence of the viscosity of SSL/chitosan complexes-stabilised emulsions at 20°C; SSL 0.4% (w/w) chitosan; 0-0.48% (w/w).

Emulsions (10% w/w oil) were made at pH 5.7 by using the preformed complexes that consisted of SSL 0.4% w/w and different amounts of chitosan. None of the emulsions that were examined exhibited a gel-like behaviour since in all cases the G' (storage modulus) was lower that G'' (loss modulus). As shown in Fig. 1, all the samples exhibited a Newtonian-like behaviour over the range of shear rates employed. However, as the content of chitosan in the complexes increased, the viscosity of the samples is raised. This may be important towards the creaming stability of the emulsions, since it has an impact on the diffusion rate of droplets and flocs [7].

The purpose of the freeze-thawing experiments was to examine the effect of this process on the stability of the emulsions made by using complexes of different SSL/chitosan ratios as emulsifying agents. In all preparations the SSL concentration remained constant (0.4% w/w), while the chitosan varied between 0-0.48 w/w. As it can be seen in Fig. 2, the sample that was stabilised solely by pure SSL was very sensitive to the freeze-thawing cycle. On the other hand, the use of SSL/chitosan complexes as surface active agents, especially the ones that originated from mixtures that contained more than 0.32% chitosan, resulted in an improved stability under these environmental stresses. Phase separation events and the creation of an oily phase on the top were observed for the reference samples (chitosan-free), while this was not the case for the emulsions with the interfaces stabilized by the SSL/chitosan complexes. Similar behaviour has been observed in the past for layer-by-layer stabilised emulsions, and several protective mechanisms were proposed [8]. The enhanced thickness of the emulsions droplets seems to

offer extra protection against rupture from the fat or the ice crystals being formed under the freezing conditions [1]. Similar behaviour was also observed when a thermal treatment was applied (90°C for 30min), confirming findings from previous studies [8].

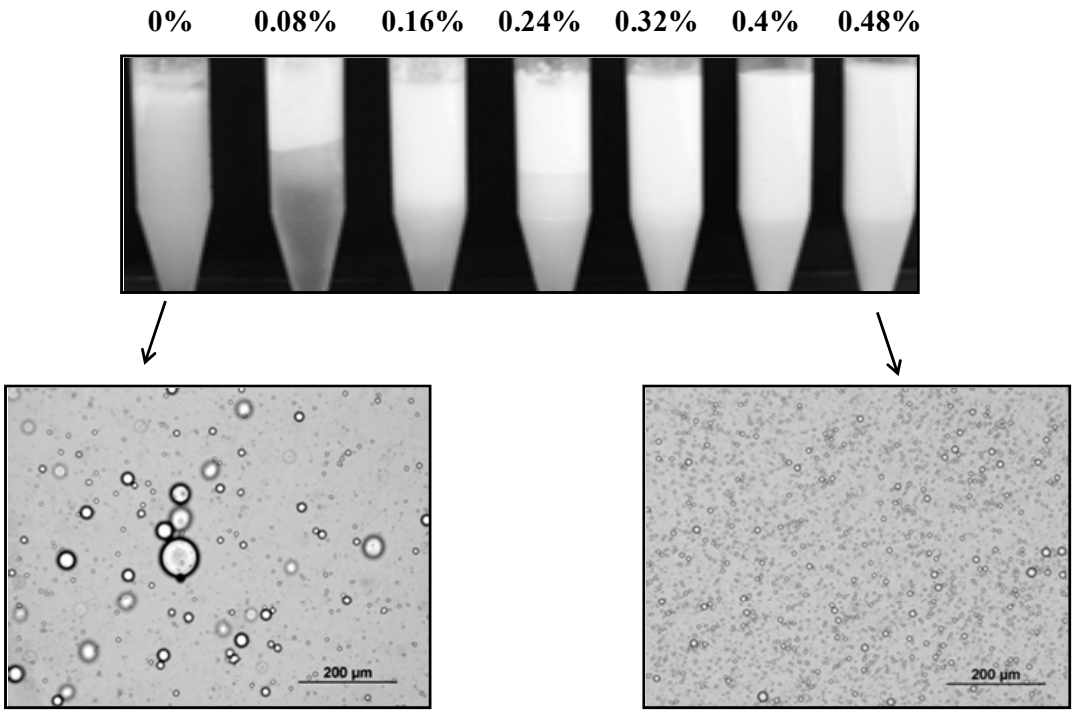

Fig. 2. Effect of the freeze-thawing process on the overall appearance and the microstructure of oil-in-water emulsions stabilised by SSL/chitosan complexes: SSL 0.4% (w/w), chitosan 0-0.48% (w/w).

4. Conclusion

This study has indicated that the stability of conventional SSL-stabilized emulsions towards droplet aggregation and coalescence, as induced by environmental (thermal) stresses, can be improved by the use of SSL/chitosan complexes as surface active agents, instead. This is a simple and low cost alternative that can be further applied to develop emulsions that function as effective delivery systems of sensitive bioactive ingredients, capable to sustain the harsh environmental conditions often encountered during food processing and storage.

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