

Formation of nano and microstructures by polysorbate–chitosan association

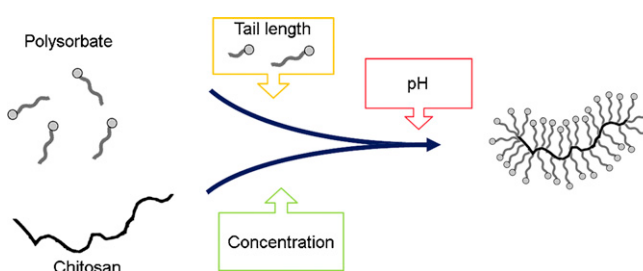
Carolina Siqueira Franco Picone, Rosiane Lopes Cunha*

Department of Food Engineering, Faculty of Food Engineering, University of Campinas (UNICAMP), 13083-862, Campinas, SP, Brazil

HIGHLIGHTS

- ▶ Nano and gel-like structures were formed by polysorbate-80 self-assembly.
- ▶ Polysorbate-20 tended to form nano sized assembled structures.
- ▶ The pH did not significantly affect the Polysorbate-20 assembled structures.
- ▶ An increase in chitosan concentration led to smaller particles.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 6 September 2012
 Received in revised form 9 November 2012
 Accepted 10 November 2012
 Available online 20 November 2012

Keywords:

Self-assembly
 Chitosan
 Polysorbates
 Nanostructures
 Microstructures

ABSTRACT

Different environmental conditions and polysorbate types were explored for the formation of nano and microstructures in association with chitosan. Systems composed of polysorbates (0–90% (w/v)) and an aqueous phase (10–90% (w/v)) containing polysaccharide (0.01–1% (w/v)) or not, were studied. First the effect of the hydrophobic polysorbate tail length on the properties of the self-assembled structures was evaluated, in order to determine the best component for interaction with the chitosan. The effect of pH (3 or 6.7) on such structural formations was then determined. Finally, the effect of chitosan concentration on the surfactant–polymer association was evaluated. The structures were characterized using rheological and conductivity measurements and by optical polarized microscopy, and their size was evaluated by dynamic light scattering. Polysorbate-20 tended to form nanoparticles whilst gel-like structures were observed in polysorbate-80 systems, which made it difficult to associate with the chitosan. Thus, the mixed systems were composed of polysorbate-20–chitosan. Structures with similar rheological properties, electrical conductivity and size were obtained with polysorbate-20 at both pH 3 and 6.7, therefore the mixed samples were prepared at pH 3, where the chitosan solubility was higher. Increasing the chitosan concentration in the mixed systems resulted in smaller and less polydispersed particles, due to the decrease in molecular mobility of the systems. These results suggest that nanoparticles with potential use for bioactive delivery could be formed by polysorbate–chitosan association.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Surfactant based delivery systems are promising vehicles for bioactive encapsulation due to the wide range of structures that can be obtained: from nanometric structures such as micelles, to complex structures such as liquid crystals. This versatility allows for their application in distinct products or even in the improvement of

product texture. Moreover, the amphiphilic character of surfactants allows the entrapment of either hydrophilic or hydrophobic bioactive compounds, increasing their dissolution in the final product [1].

Surfactant self-assembled structures change in size and shape with surfactant concentration, temperature, pH, pressure [2,3] and in the presence of biopolymers [4,5]. Chitosan is a polysaccharide with great potential in the food industry and in biotechnological applications, due to its biodegradability and biocompatibility [4,6]. It is an effective material in delivery systems due to its muco-adhesive properties which favor its bioactive adsorption by epithelial tissues [7]. Chitosan is a cationic polyelectrolyte which

* Corresponding author. Tel.: +55 19 3521 4047; fax: +55 19 3521 4027.
 E-mail address: rosiane@fea.unicamp.br (R.L. Cunha).

carries free amino and hydroxyl groups along its backbone. The pK_a value of the free amino groups is around 6.5, which accounts for its pH dependent solubility [8]. The deacetylation degree of the chitosan and/or its solution conditions have an impact on the charge density along the chains, and therefore on its flexibility and conformation [9,10]. These properties, together with the hydrophobicity of the backbone, play an important role in chitosan–surfactant interactions [11]. Despite the marked importance of chitosan and nonionic surfactants, very little is known about the assembly and physicochemical properties of these polymer/surfactant pairs. Most of studies on polymer/surfactant pairs are concerned with synthetic polymers and surfactants which cannot be applied in food products [4,12,13].

Polysorbates are non-ionic surfactants widely used in food products. They are derived from PEG-ylated sorbitan (hydrophilic group) esterified with fatty acids (hydrophobic group), with a total of 20 ethylene oxide subunits per molecule. The hydrocarbon chains provide the hydrophobic nature of the polysorbates, while the hydrophilic nature is provided by the ethylene oxide subunits [14,15]. The different polysorbates vary in the length of the polyoxyethylene chain, type of fatty acid, and degree of esterification [16]. Such variety results in different self-assembly mechanisms and structures.

The aim of this work was to form nano and microstructures by assembly of polysorbates and chitosan. Different concentrations of water (10–90% (w/v)), polysaccharide (0.01–1% (w/v)) and surfactants (0–90% (w/v)) were studied. The effect of the hydrophobic polysorbate tail length on the properties of the self-assembled structures was initially studied, in order to determine the best component for interaction with the chitosan. The effect of pH (3.0 or 6.7) on such structures was then determined. Finally, the effect of chitosan concentration on the surfactant–polymer assembly was evaluated. The structures were characterized using rheological measurements and optical polarized microscopy. The conductivity and size of the structures were evaluated by dynamic light scattering.

2. Experimental

2.1. Materials

Polyoxyethylene sorbitan monolaurate and polyoxyethylene sorbitan monooleate also known as polysorbate-20 (Tween-20) and polysorbate-80 (Tween-80), respectively, were purchased from Synth (Brazil). The schematic molecular structures of the surfactants are shown in Fig. 1. Low molar mass (150 kDa) chitosan with a degree of deacetylation of 75–85% was obtained from Sigma–Aldrich (St. Louis, USA) and used without further purification.

2.2. Preparation of self-assembled systems

The samples were prepared by mixing the surfactant in the aqueous phase for 10 min with magnetic stirring and then storing them at 25 °C for 4 days for structure stabilization. The

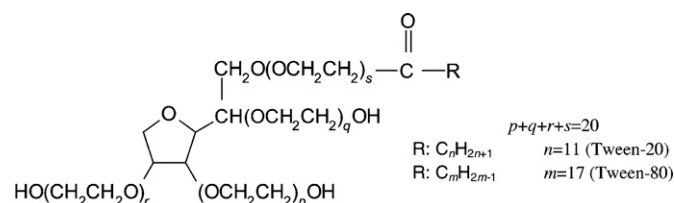


Fig. 1. Molecular structures of the polysorbates.

concentration of the polysorbates was varied from 0 to 90% (w/v) in 10% steps (w/v). Pure polysorbate solutions were also analyzed. The role of the length of the hydrophobic polysorbate tail was evaluated using samples composed of pure deionized water (pH 6.7) and either polysorbate-20 or polysorbate-80. In addition, the effect of the pH of the aqueous phase was determined using 100 mM sodium acetate buffer (pH 3) as the aqueous phase in the polysorbate-20 systems.

The chitosan stock solution (2%, w/v) was prepared by dissolution of the chitosan powder in 100 mM sodium acetate buffer (pH 3) and stirring overnight at 25 °C. The mixed samples containing chitosan in the aqueous phase were prepared by magnetic stirring of the chitosan stock solution with polysorbate and 100 mM sodium acetate buffer (pH 3) at 25 °C for 10 min. The final concentration of chitosan in the samples was set at 0.01, 0.1, 0.5 or 1% (w/v). Since the concentration of the chitosan stock solution could not be increased (due to its high viscosity), mixed samples containing 0.5 and 1% chitosan as well as surfactant concentration higher than 80 and 50% polysorbate-20 could not be prepared.

2.3. Electrical conductivity, zeta potential and particle size distribution

The electrical conductivity, zeta potential and size distribution were measured by dynamic light scattering (DLS) in a Zetasizer Nano-ZS (Malvern Instruments, Herrenberg, Germany) with a detection angle of 173°. All measurements were carried out at 25 °C.

2.4. Rheological measurements

The rheological properties of the samples were determined in an AR 1500 controlled stress rheometer (TA Instruments, England). A stainless steel cone and plate geometry with a diameter of 60 mm was used.

2.4.1. Flow curves

Flow curves were obtained by an up–down–up steps program with shear rate ranging from 0 to 300 s^{-1} at 25 °C. The data obtained in the third sweep were fitted to the power law equation (Eq. (1)) using the Rheology Advantage Data Analysis v. 5.7.0 software (TA Instruments, USA).

$$\sigma = k\dot{\gamma}^n \quad (1)$$

where σ is the shear stress (Pa), $\dot{\gamma}$ the shear rate (s^{-1}), k the consistency index (Pa s) and n the flow behavior index (dimensionless). The apparent viscosity (η_{70}) of the non-Newtonian samples was determined at 70 s^{-1} since some samples showed structure breakdown at higher shear rates.

2.4.2. Oscillatory measurements

The effect of temperature on the samples with gel-like behavior was evaluated by oscillatory rheological tests. The shear strain was kept at 1% to assure that the measurements were carried out within the linear viscoelastic region. The samples were gently poured onto the rheometer plate, melted at 60 °C per 2 min, and then cooled to 25 °C at 1 °C/min and 0.1 Hz. The melting temperature was chosen to be below the cloud point of both polysorbates, 76 and 65 °C for polysorbate 20 and 80 respectively [17]. Changes in the slope of the complex viscosity (η^*) vs. temperature curves were maximized from the derivation of the data obtained using the Savitzky and Golay filter [18]. The gelation point was determined as the temperature of the maximum (absolute) slope of $\log(\eta^*)$.

Download English Version:

<https://daneshyari.com/en/article/593847>

Download Persian Version:

<https://daneshyari.com/article/593847>

[Daneshyari.com](https://daneshyari.com)