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Development and rheological properties of ecological emulsions formulated with a biosolvent and two microbial polysaccharides

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ABSTRACT

The influence of gum concentration and rhamsan/welan gum ratio on rheological properties, droplet size distribution and physical stability of eco-friendly O/W emulsions stabilized by an ecological surfactant were studied in the present work. The emulsions were prepared with 30 wt% α-pinene, a terpenic solvent and an ecological alternative for current volatile organic compounds. Rheological properties of emulsions showed an important dependence on the two studied variables. Flow curves were fitted to the Cross model and no synergistic effect between rhamsan and welan gums was demonstrated. Emulsions with submicron mean diameters were obtained regardless of the gum concentration or the rhamsan/welan ratio used. Multiple light scattering illustrated that creaming was practically eliminated by the incorporation of polysaccharides. The use of rhamsan and welan gums as stabilizers lead to apparent enhancements in emulsion rheology and physical stability.

1. Introduction

Oil-in-water emulsions are thermodynamically unstable systems that consist of oil droplets dispersed in an aqueous phase. They tend to separate into two layers over time through some physicochemical mechanisms such as creaming, coalescence, flocculation and/or Ostwald ripening [1]. Thus, in order to obtain kinetically stable emulsions for a reasonable period of time, their formulation requires the incorporation of substances known as emulsifiers and/or thickening agents [2]. In addition, the role of green solvents in the chemical and pharmaceutical industries is becoming increasingly important [3]. α-Pinene is a renewable biosolvent, which may be obtained from pine resins or distillation. This terpene is used as an insecticide, solvent and perfume base, as well as for the synthesis of camphor. α-Pinene is completely miscible with oils and insoluble in water [4].

Polysaccharides are widely used as thickening, stabilizing and emulsifying agents for their biocompatibility, biodegradability and non-toxicity [5]. There are different mechanisms by which these polymers can stabilize an emulsion [6]. The efficiency depends on the concentration of hydrocolloids in the aqueous phase and on the characteristics of the structure formed by the biopolymer [1]. The use of hydrocolloid mixtures can display both synergistic and antagonistic effects [7]. When two different polysaccharide solutions are mixed, enthalpic interactions between chains of different types may be more favorable (associative interactions) or less favorable (segregative interactions) than interactions between chains of the same type [8].

Microbial polysaccharides can be manufactured under controlled conditions, resulting in commercial batches with outstanding reproducibility of their functional properties. Sphingans from *Sphingomonas* sp., for example gellan, welan or rhamsan, are structurally closely related microbial polysaccharides having similar backbone structure except for the location of side chains [9,10]. This difference, however, has a profound influence on their behavior in aqueous media. Thus, whereas gellan can form stable gels in the presence of salts, neither rhamsan nor welan give true gels, but only weak gels or very viscous solutions with a high degree of thermal, pH and salinity stability [11]. These gums act as thickening, suspending, binding and stabilizing agents and have commercial application in food, ink, petroleum and other industries [12,13]. However, there is still very little work reported on the use of rhamsan and welan gums as a stabilizer of oil-in-water emulsions, and the rheological behaviors of the resultant emulsions have not been previously reported.

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When such polysaccharide solutions are employed to thicken the continuous phase of an emulsion, other components should also be added to the solution as emulsifying agents, the most important being surfactants. Polyoxyethylene glycerol esters derived from cocoa oil are non-ionic surfactants obtained from a renewable source which fulfill the environmental and toxicological requirements to be used as emulsifying agents [14]. These surfactants are fully innocuous for human skin and hair and their properties are appropriate for the design of eco-friendly products [15,16]. The role of surfactants is essential to provide long-term stability to emulsions, since they prevent droplet coalescence by adsorbing at the o/w interface and increasing the repulsive interactions among droplets. Interactions between surfactants and polysaccharides can affect the macroscopic properties of emulsions. These interactions may occur by distinct mechanisms that depend on the chemical composition of the polymer chain, the nature of the surfactant and on the electrical charges involved [17].

To obtain an emulsion with good rheological and stabilizing properties, the choice of the constituent components and their concentrations should be made carefully. This study focuses on emulsions formulated with a green solvent (α-pinene) as dispersed phase, an eco-friendly surfactant as emulsifier and two microbial polysaccharides as stabilizers and thickeners. These emulsions may find applications related to the design of biotechnological complex systems with different uses. This work could be considered the continuation of the previously reported article by Trujillo-Cayado et al. [18].

2. Materials and methods

2.1. Materials

α-Pinene (0.84 g/mL at 25 °C) was purchased from Sigma–Aldrich®. Industrial grade welan gum (K1A96) and rhamsan gum (K2C401) were used as supplied by CP Kelco Company (San Diego, USA). Sodium azide (0.1 wt% in the final formulation) was added to the samples to prevent the growth of microorganisms.

A commercial polyoxyethylene glycerol ester surfactant derived from cocoa oil was used; namely Levenol® C201 (Glycereth-17 cocoate), which is a technical grade surfactant with 17 ethylene oxide groups. This material was kindly provided by KAO and used as received. The solutions were prepared with deionized water.

2.2. Methods

2.2.1. Preparation of aqueous solutions

The gum solutions were prepared by slowly dispersing gums in deionized water at room temperature. Subsequently, they were mechanically stirred using a Eurostar Digital (IKA Labortechnik, Germany) for three hours. When a homogeneous phase was achieved, then Levenol C201 was added. Three batches of each aqueous solution with a final weight of 250 g were prepared.

2.2.2. Preparation of emulsions

Oil-in-water emulsions using α-pinene as dispersed phase were prepared using a rotor-stator device (Ultraturrax T25, dispersion element KV09-93), at 9500 rpm for 120 s. Dispersed phase concentration in the emulsion was fixed at 30 wt%. Surfactant concentration was also fixed at 3.5 wt%. The effect of two formulation variables on emulsion properties was investigated. Six emulsions were prepared using different gum concentrations (0.33, 0.56 and 0.80 wt%) and rhamsan/welan gum ratios (100/0, 50/50 and 0/100) as can be seen in Table 1. Additionally, an emulsion without gum was prepared. Three replicates of each emulsion with a final weight of 300 g were prepared.

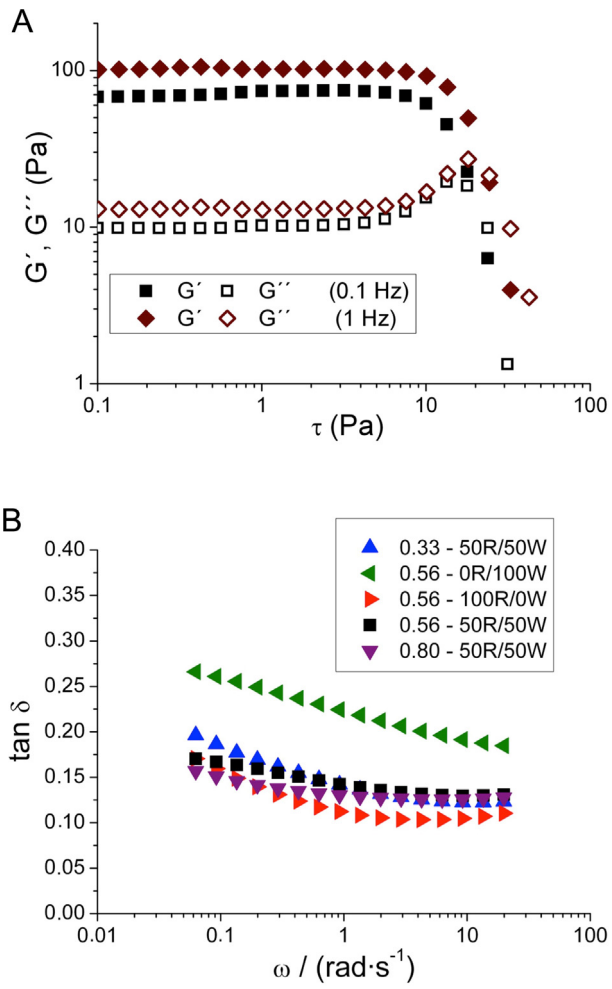

Fig. 1. (a) Oscillatory shear stress sweeps as a function of frequency for the emulsion 0.56-50R/50W and (b) loss tangent values as a function of gum concentration and rhamsan/welan gum ratio for all emulsions. Temperature: 20 °C.

Table 1
Values of gum concentration and rhamsan/welan gum ratio for all studied emulsions. R: rhamsan gum, W: welan gum.

Name	Gumconcentration (wt%)	Rhamsan/welangum ratio
Without gum	0.00	–
0.56–50R/50W	0.56	50/50
0.56–0R/100W	0.56	0/100
0.56–100R/0W	0.56	100/0
0.33–50R/50W	0.33	50/50
0.80–50R/50W	0.80	50/50

2.2.3. Rheological characterization

The rheological characterization involved stress and frequency sweeps in small amplitude oscillatory shear experiments (SAOS) and steady shear flow tests. Rheological experiments were conducted with a Haake MARS III controlled-stress rheometer (Thermo-Scientific, Germany), using a serrated plate–plate sensor (60 mm diameter, gap: 1 mm) to prevent wall slip effect as recommended by Barnes [19].

Stress sweeps were performed in a range of 0.1–100 Pa at two different frequencies: 0.1 Hz and 1 Hz. Frequency sweep tests (from 20 to 0.05 rad s^{-1}) were performed by selecting a stress within the linear range. Equilibration time prior to rheological tests was 5 min. Small amplitude oscillatory shear experiments at 1 Hz, as a function of time, were carried out to estimate the equilibration time for the emulsion 0.56–50/50 by way of example.