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Rheological behavior of aqueous dispersions containing blends of rhamsan and welan polysaccharides with an eco-friendly surfactant

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ABSTRACT

Small amplitude oscillatory shear and steady shear flow properties of rhamsan gum and welan gum dispersions containing an eco-friendly surfactant (a polyoxyethylene glycerol ester) formulated to mimic the continuous phase of O/W emulsions were studied using the surface response methodology. A second order polynomial equation fitted the influence of surfactant concentration, rhamsan/welan mass ratio and total concentration of polysaccharides. Systems containing blends of rhamsan and welan did not show synergism but thermodynamic incompatibility and made it possible to adjust the linear viscoelastic and low shear rate flow properties to achieve values in between those of systems containing either rhamsan or welan as the only polysaccharide.

All the systems studied exhibited weak gel rheological properties as the mechanical spectra displayed the plateau or rubber-like relaxation zone, the linear viscoelastic range was rather narrow and flow curves presented shear thinning behavior, which fitted the power-law equation. While mechanical spectra of the systems studied demonstrated that they did not control the linear viscoelastic properties of the corresponding emulsions, the blend of rhamsan and welan gums was able to control the steady shear flow properties.

1. Introduction

Blends of non-adsorbing polysaccharides, namely rhamsan and welan gums, along with a polyoxyethylene glycol ester nonionic surfactant, can be successfully used to prepare concentrated α-pinene in water emulsions, as has recently been reported by this research team [1].

Polysaccharides are widely used in different industrial fields since they have an amazing variety of applications depending on their chemical structure. They may provide thickening, water-holding, stabilizing, chelating, emulsifying, gelling, coating, adhesive and film-forming properties. In addition some of them are used as scaffolds in biomaterials, drug-delivery system, sponge-like matrices and texturized products [2–6].

Non-adsorbing polysaccharides are used in O/W emulsions as stabilizers due to their capacity to control not only the viscosity of the continuous phase but also its viscoelasticity. Natural polysaccharides insofar as they are biopolymers have advantages over synthetic stabilizing polymers, such as acrylic polymers [7], since they contribute to the biodegradability of emulsions and are safe for human consumption and use in food, cosmetic, agricultural and health-related applications.

Microbial polysaccharides are an interesting alternative to other natural gums whose properties may be more batch-dependent (seaweed, exudate, seed, plant extract gums) or whose price and supply may be rather unstable, such as those of guar gum and gum Arabic [4,8,9].

Rhamsan and welan gums are heteropolysaccharides called Sphingans since they are produced from bacteria of the genus Sphingomonas, namely from *Alcaligenes* sp. ATCC 31961 and ATCC 31555, respectively. Sphingans also involve gellan and diutan gums. All of them have a repeating unit consisting of a straight tetrasaccharide based on d-glucose, d-glucuronic and l-rhamnose in a molar ratio of 2:1:1, but with different side chains [10]. However, this yields marked differences in the behavior of their respective aqueous dispersions. Therefore, while the main applications of gellan gum rely on the formation of gels [8] or fluid gels [11–13], welan and rhamsan gums form weak gels and find applications as thickening and stabilizing agents mainly in cement systems, agrochemical and coating products [14–17]. In addition, rhamsan gum has been used

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as a clay flocculating agent, in the formulation of injectable gels for plastic surgery and, like welan gum, is considered a food additive in Japan [18–20]. Welan is potentially interesting for oil-well drilling and enhanced oil recovery (EOR) formulations because of its stability under high temperature and salinity [21]. Furthermore, welan has recently been reported to form composites with graphene oxides and carbon nanotubes, showing promising properties as adsorbents [22,23]. If compared with xanthan gum, which is the standard stabilizing polysaccharide, rhamsan and welan aqueous dispersions show greater viscosity and better temperature stability, respectively [15,24].

Surfactants play a relevant role in the formulation and formation of emulsions since they exert a pronounced effect on interfacial properties and therefore on the droplet size distribution [25]. Even though most of the surfactant molecules in emulsions are located at the interface, excess amounts of surfactants may also be found in the continuous phase forming micelles and promoting depletion flocculation among droplets. This may be prevented by a high viscous continuous phase upon forming structured aggregates of surfactants and/or by the presence of a polysaccharide at a sufficiently high concentration to form a weak gel structure [4,26].

Non-ionic surfactants have the advantage that their behavior as emulsifiers is not affected by the ionic strength and also that they promote a steric stabilization mechanism in emulsions. Polyoxyethylene glycerol esters derived from coconut oil are non-ionic surfactants obtained from a renewable source. Furthermore, their use has led to great interest due to the overproduction of glycerine in the biodiesel industry [27]. Interestingly, these surfactants fulfill the environmental and toxicological requirements permitting their use as eco-label materials in Europe [28]. Their excellent wetting, interfacial and emulsifying properties are well documented [29–32]. These surfactants are fully innocuous for human skin and hair and their properties are appropriate for the design of eco-friendly products [33]. On the whole, interactions between surfactants and polysaccharides depend on the chemical composition of the biopolymer and surfactant molecules as well as on the electrical charges involved [34,35]. For polyoxyethylene glycerol ester surfactants, the interactions with anionic polysaccharides, like rhamsan and welan gums, must essentially be based on a competition mechanism for structuring water on account of their non-ionic nature. On top of that, this interaction will obviously depend on the hydrophilic-lipophilic balance number (HLB) of the polyoxyethylene glycerol ester used.

The objective of this research was to study the rheology of aqueous dispersions of rhamsan, welan and a polyoxyethylene glycerol non-ionic surfactant formulated as model continuous phases of 30% O/W emulsions whose behavior has been previously reported [1]. More specific aims were to discover how far the rheology of the continuous phase controls the rheology of the corresponding emulsions and to study the influence of surfactant and total polysaccharide concentrations as well as of the rhamsan/welan mass ratio on the rheology of these systems.

2. Materials and methods

2.1. Materials

Commercial industrial grade welan gum (K1A96) and rhamsan gum (K2C401) were used as supplied by CP Kelco Company (San Diego, USA). 0.1 wt% sodium azide was added to the final formulation to prevent the growth of microorganisms.

A commercial polyoxyethylene glycerol ester surfactant derived from coconut oil was used. Namely Levenol® C-201 (Glycereth-17 cocoate), which is a technical grade surfactant with an average of 17 ethylene oxide groups and a hydrophilic-lipophilic balance (HLB) number of 13. This surfactant was kindly provided by KAO Chemicals Europe (Barberá del Vallés, Spain) and used as received. The dispersions were prepared with deionized water.

2.2. Methods

2.2.1. Preparation of aqueous dispersions

Gum dispersions were prepared by slowly dispersing the required amount of gum in deionized water at room temperature. A blend of powdered rhamsan and welan gums were used to prepare dispersions containing both gums. Subsequently, they were mechanically stirred using a Eurostar Digital homogenizer (IKA Labortechnik, Germany), equipped with a propeller of diameter 40 mm, at 700 rpm for 3 h until a homogeneous phase was achieved. Levenol® C-201 was then added and mixed at 300 rpm for 30 min.

2.2.2. Rheological characterization

The rheological characterization involved stress and frequency sweeps in small amplitude oscillatory shear experiments (SAOS) and stepwise 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 [36]. 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 amplitude within the linear range.

Flow curves were determined by a stepwise increasing controlled-stress protocol with 0.01% approximation to steady-state response as a set point with a cut-off criterion of 3 min/point. Shear rates were calculated at the rim of the parallel plate geometry, using Rheowin 4.0 software.

Equilibration time prior to rheological tests was 5 min. The results shown correspond to dispersions aged for 24 h and represent the mean of three measurements. All measurements were carried out at 20 °C ± 0.1 °C.

2.2.3. Experimental design and data analysis

The effects of three variables on rheological properties were studied using central composite design and surface response methodology.

Surface response methodology is an efficient statistical technique particularly appropriate for the optimization of formulations or processing [37–39]. This technique overcomes the limitations of single parameter formulation, which is both time-consuming and cannot assess the complex interactions among various parameters [40].

The independent variables considered were surfactant concentration (x_1), total polysaccharide concentration (x_2) and the rhamsan/welan gum mass ratio (x_3). These three independent factors were studied at five different levels (−1.68, −1, 0, +1 and +1.68) selected on the basis of preliminary experimental work. Surfactant concentration and the total gum concentration ranged respectively from 0 to 10 wt% and from 0.464 to 1.136 wt%, according to the composition of emulsions previously studied [1] (see Table 1). The rhamsan/welan mass ratio (R/W) was studied in the range 0–1, where 0 means 100 wt% of welan gum and 1 means 100 wt% of rhamsan gum.

Experimental data were fitted to the following second-order polynomial model.

$$Y = \beta_0 + \beta_i x_i + \beta_{ii} x_i^2 + \beta_{ij} x_{ij} \text{i, j=1, 2, 3} \quad (1)$$

where Y is the response variable, β_0 is the constant, β_i is the coefficient for the linear effect, β_{ii} is the coefficient for the quadratic effect, β_{ij} is the coefficient for the interaction effect, and x_i and x_j are the coded independent factors. The quadratic equation (Eq. (1))