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METHODOLOGY FOR THE DEVELOPMENT OF ECOLOGICAL EMULSIONS FORMULATED WITH GREEN SOLVENTS OR ESSENTIAL OILS

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RESUMEN

Las emulsiones ecológicas se formulan y preparan idealmente siguiendo los principios del desarrollo sostenible o la química verde. Estas emulsiones verdes poseen un gran número de aplicaciones, ya que por ejemplo son utilizadas en la industria alimentaria. La industria química está mostrando especial atención a la sustitución de los disolventes sintéticos por disolventes ecológicos en el desarrollo de emulsiones aceite-en-agua para usos agroquímicos, como pinturas, tintas de impresión, desengrasantes y como limpiadores. Los disolventes ecológicos se utilizan cada vez más como consecuencia de la prohibición de algunos disolventes orgánicos tradicionales y sintéticos. Por este motivo, los científicos e ingenieros responsables del desarrollo de productos están afrontando el desafío de formular emulsiones que contienen nuevos disolventes, tensioactivos o aditivos obtenidos a partir de fuentes renovables y con buenas propiedades ecológicas. En este capítulo se desarrolla una metodología para el desarrollo de emulsiones ecológicas con componentes obtenidos a partir de fuentes renovables, de nula toxicidad y biodegradables como una alternativa sostenible a aquellos productos que contienen disolventes orgánicos tradicionales.

Palabras clave: *Disolvente verde, emulsión, reología, química verde, tensioactivo.*

ABSTRACT

Green emulsions are formulated and ideally prepared under the principles of the so-called sustainable development or green chemistry and find a great variety of applications. These systems are increasingly used by the food industry insofar as there is an increasing tendency to reduce the number of synthetic additives and to increase the use of biomaterials and ingredients with functional properties. For similar reasons they are more and more used by the pharmaceutical and cosmetic industries. The chemical industry is also paying attention to the substitution of synthetic solvents by green solvents in water-based emulsions used as agrochemicals, paints, printing inks, fat removers and all-purpose cleaners. Green solvents are increasingly used since many synthetic solvents have been banned due to their carcinogenic or toxic properties and to their poor biodegradability. For this reason, scientists and engineers responsible for product development face the challenge to formulate emulsions containing new solvents, surfactants and additives obtained from renewable raw materials and exhibiting enhanced ecological properties.

Keywords: *Emulsion, green solvent, green chemistry, rheology, surfactant.*

INTRODUCTION

The objective of green chemistry is to achieve sustainability through science and technology. The 3rd, 7th and the 10th principles of Green Chemistry are related to the use of safer and eco-friendly formulations. The use of traditional organic solvents in agrochemical formulations has been restricted since they posed health hazards for farmers and because of its harmful effects on the environment (Anastas et al., 1998). Therefore, the chemical industry is paying more and more attention to eco-friendly or better, green solvents. These solvents not only must derive from renewal resources and exhibit enhanced biodegradability but also must possess the expected functional properties. Water-based formulations are by far preferred to oil-based ones for ecological reasons. The non-polar character of most organic solvents prevents their incorporation into aqueous homogeneous solutions due to thermodynamic incompatibility. Thus, they first have to be converted into a colloidal dispersion consisting for instance of an oil phase dispersed as small droplets within an aqueous phase.

This work highlights that rheology is a powerful tool for emulsion engineering if used cooperatively with different techniques, such as optical microscopy (bright field, polarising microscopy, phase contrast), confocal scanning laser microscopy (CSLM) and scanning electron microscopy (SEM, cryo-SEM), laser diffraction, and multiple light scattering. Therefore, the role of rheology to detect and control destabilization by creaming as well as to understand oil flocculation, coalescence and Ostwald ripening will be assessed.

METHODOLOGY

The scope of this work involves formulations based on different green solvents, eco-label surfactants, copolymers, hydrocolloids and clays. The composition of the oil phase has a major influence on the formation and stability of emulsions. N,N-dimethyldecanamide (Agnique® AMD-10, BASF) is considered as an eco-friendly solvent which may find applications in matrices for agrochemical products (Bigorra, 2010). D-Limonene, a natural hydrocarbon, is a biosolvent derived from the rinds of citrus fruits such as grapefruit, lemon, lime, and, in particular, oranges. Another monoterpene susceptible to be an interesting alternative solvent is α-pinene. It represents the major constituent of turpentine oils from most conifers and a component of the wood and leaf oils obtained from plants such as rosemary or parsley. Thyme oil has antiseptic and antibacterial properties so that it may be used in cleansing and cosmetic formulations. Sweet fennel oil can be used in food systems.

Ecological surfactants have attracted much attention recently. We report here results of emulsions formulated with surfactants that exhibit the European eco-label; namely, a) an alkyl (C14-C18) poly-pentoside (Appyclean™ 6548, Wheatoleo) derived from wheat biomass and b) a polyoxyethylene glycerol ester (Levenol™ C-201, KAO) derived from coconut oil. In addition, results of emulsions formulated with amphiphilic copolymers (Atlas™ G-5000 and Atlox™ 4913, Croda) are also reported.

Organic (gum polysaccharides) and inorganic (clays) stabilizers have been used to extend the shelf-life of emulsions studied. Their ability to increase the viscosity of a solution depends principally on their molecular characteristics (molecular weight, conformation, etc.).

We have used several microbial polysaccharides, Welan, Rhamsan, Xanthan, Gellan and Diutan gums, kindly provided by CP-Kelco. In addition, a fumed silica (Aerosil™ 200, Evonik) and a clay based on sepiolite (Pangel™ S9, Tolsa) were used as inorganic stabilizers.

RESULTS AND DISCUSSION

The rheology of emulsions from both a fundamental and an applied point of view is an important tool to characterize green emulsions. A huge amount of emulsions must be formulated and processed such that they are classified as “flowable materials” showing submicron mean droplet sizes. For this reason, the scope of this work involves the use of formulations based on different green solvents, eco-label surfactants, copolymers, hydrocolloids and clays.

Rheology is directly related to the structure of dispersed systems. For instance, an analysis of flow curves in emulsions formulated with Agnique® AMD-10 and d-limonene or α-pinene with very similar droplet size distributions allowed different flocculation grades to be detected (Santos et al., 2016a; Trujillo-Cayado et al., 2016a). In addition, this fact could be checked by analysing the corresponding mechanical spectra detected (Santos et al., 2015; Trujillo-Cayado et al., 2017a). The “flowable” properties of these emulsions, formulated with mixtures of green solvents, were supported by their apparent viscosity values. The study of zero shear viscosity is a great tool to differentiate between destabilization mechanisms in emulsions. The drop of zero shear viscosity with aging time is a clear indication of droplet size increase for emulsions detected (Santos et al., 2014; Santos et al., 2015; Trujillo-Cayado et al., 2016a; Trujillo-Cayado et al., 2017b). In addition, an analysis of the evolution of the plateau modulus can detect coalescence in dispersed systems. In fact, a decrease in this parameter with aging time was shown by concentrated green emulsions undergoing coalescence, as indicated by laser diffraction (Santos et al., 2016b). By contrast, the creaming process involves an increase in zero shear viscosity and a decrease in the flow index with aging time, provided sampling is made from the middle or upper part of the container (Trujillo-Cayado et al., 2017b). Creaming occurs when gravitational separation outweighs the free movement of droplets. Rheology was an important tool to study the influence on emulsion properties and physical stability of several formulation variables like ratio of solvents (Santos et al., 2014), surfactant concentration (Pérez-Mosqueda et al., 2014; Santos et al., 2015; Trujillo-Cayado et al., 2017) or dispersed phase concentration (Santos et al., 2015; Trujillo-Cayado et al., 2017b). Furthermore, rheology was able to distinguish between different processing variables (Santos et al., 2016b) and emulsification methods (Trujillo-Cayado et al., 2016a). On top of that, the analysis of the viscoelastic properties can suggest the occurrence of different structures in emulsions formulated with different eco-friendly surfactants and detect destabilization mechanisms like depletion flocculation. An excess of free micelles in the continuous phase is expected to trigger depletion flocculation, influencing the rheological properties of the emulsion. This rheological change may be due either to an increase in viscosity of the continuous phase and/or the formation of a stronger oil network due (Pérez-Mosqueda et al., 2014; Santos et al., 2015; Trujillo-Cayado et al., 2017b. In addition, longer relaxation times may be associated to stronger droplet−droplet interactions, which can be correlated with longer macroscopic stability against creaming in emulsions.

Given that the rheology of many "flowable" emulsions is controlled by the rheology of the continuous phase, different case studies will be discussed. In this way, relevant examples of the rheology of polysaccharide solutions, weak gels, fluid (sheared) gels and suspensions of clays will be analysed. Fluid gels prepared with low-acyl gellan gum and either Na^+ or Ca^{2+} can be used as dispersion stabilizers due to the fact they show a high zero-shear viscosity and a dominant elastic response when linear viscoelastic behavior is guaranteed. As a consequence, in the quiescent state, fluid gels exhibited a structural network. Fluid gel microstructure tends to break progressively down as shear stress increases. Thus, these materials exhibited time-dependent flow properties before reaching steady state response. For this reason, their thixotropic properties must be assessed in order to evaluate their role as dispersion stabilizer. Rheological properties of low-acyl gellan gum samples with promising applications as emulsions stabilizers have been reported in several fairly recent articles (García et al., 2011; García et al., 2015; García et al., 2016).

Biopolymers are frequently used to stabilize aqueous suspensions or O/W emulsions. These polymers can stabilize emulsions through different mechanisms. Thus, the formation of an extended hydrated polymer network results in high viscosity of the continuous phase at low shear, thus slowing down the droplet motion. In addition, polymeric material may surround the oil droplets, ensuring effective steric hindrance of droplet coalescence. A combination of Gellan and Xanthan gums was utilized to achieve O/W emulsions containing α-pinene and two amphiphilic copolymers (Atlas™ G-5000 and Atlox™ 4913) (García et al., 2014). Small amplitude oscillatory shear results supported the likely occurrence of three different relaxation mechanisms and microstructures, which were dependent on hydrocolloid system used. The relaxation spectrum of the emulsion containing both polysaccharides indicated the existence of thermodynamic incompatibility between both polysaccharides. Flow curves fitted the Carreau-Yasuda model and highlighted the occurrence of negative synergism between Gellan and Xanthan gums. Furthermore, the influence of different ratios of amphiphilic copolymers (Atlas™ G-5000 and Atlox™ 4913) in emulsions formulated with Gellan gum and d-limonene or α-pinene as dispersed phase was studied. Results of these investigations indicated that the ratio of emulsifiers had significant effects on the physical stability, droplet size, viscoelasticity, and viscosity of these emulsions. An increase in Atlas™ G-5000 enhanced both the G´ and G´´ values and also the viscosity, providing higher stability to emulsions. Adding Gellan gum yielded viscoelastic spectra with a weak frequency dependence of G' and G'', according to the formation of a faint gel-like matrix.

The rheological properties of concentrated welan gum aqueous solutions with different polymer concentration have been studied at 20°C. Flow curves and mechanical spectra were determined at several gum concentrations by step-wise and SAOS tests. The results showed shear thinning behavior and weak gel-like viscoelastic behavior in the range of concentrations studied (0.1-0.6 wt%). Another interesting technique used was the parallel superposition rheology, which consists of applying steady shear in parallel with oscillatory shear. Thus, a change from weak gel-like viscoelastic behavior to fluid like viscoelastic behavior was observed when the steady shear increased. The frequency locating the G' and G'' crossover shifted to higher frequencies values as the steady-state shear stress applied was increased. In other words, increasing shear stress values resulted in decreasing terminal relaxation times, congruently with a weaker and weaker microstructure. This technique allowed obtaining linear viscoelastic snapshots while the sample microstructure was progressively disrupted.

A detailed study of the rheological properties of mixtures of Rhamsan gum and Welan gum solutions containing an eco-friendly surfactant has been reported elsewhere (Trujillo-Cayado et al., 2016b). By using a response surface methodology, the effects of surfactant concentration, Rhamsan/Welan mass ratio and total concentration of polysaccharides were investigated. A second order polynomial equation fitted the influence of surfactant concentration, Rhamsan/Welan mass ratio and total concentration of polysaccharides, the latter being the most significant variable. Systems containing blends of Rhamsan and Welan did not show synergism but made it possible to adjust the linear viscoelastic and low shear rate flow properties in order 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. Furthermore, the influence of total gum concentration and Rhamsan/Welan gum ratio on rheological properties, droplet size distribution and physical stability of eco-friendly O/W emulsions formulated with α-pinene and stabilized by an ecological surfactant were studied. Rheological properties of emulsions showed an important dependence on the two studied variables. Flow curves were fitted to the power-law model and no synergistic effect between Rhamsan and Welan gums was demonstrated. Multiple light scattering illustrated that creaming was practically eliminated by the incorporation of polysaccharides. The use of Rhamsan and Welan gums as stabilizers improved the emulsion rheology and physical stability in comparison with the formulation without gum.

Small amplitude oscillatory shear (SAOS) is a useful tool to study the viscoelasticity of a wide range of materials. This technique requires that tests are conducted within the linear viscoelastic range (LVR), which guarantees the material microstructure is not destroyed by shear. In the LVR the properties of materials can be defined by two properties storage modulus in phase with the strain G’ and viscous modulus out phase 90° with strain G”. Although this conditions of low deformation are not near real flow conditions, such as those typical of processing and transport. When the strain increases above a critical value the classic linear viscoelastic approach is no longer valid. This is due to the fact that the response is not a simple sinusoidal function and it is necessary to use another method like that proposed by We have reported the applications of LAOS for xanthan gum aqueous dispersions at different NaCl concentrations (Carmona et al., 2014) and different polymer concentration (Carmona et al., 2015). LAOS was demonstrated to be much more sensitive than small amplitude oscillatory shear (SAOS) when studying the influence of NaCl concentration. This technique allows gaining a deeper insight into the viscoelastic properties of materials under non-linear conditions, which is closer to real flow conditions. The rheological LAOS characterization was carried out by means of both full-cycle (average elastic modulus and dynamic viscosity) and local methods (strain-hardening and shear-thickening ratios) (Carmona et al., 2014). The plot of the maximum value of the local shear-thickening parameter (T) obtained by LAOS against concentration showed a change of the viscoelastic behavior associated to the modification of the gum structure.

Pangel ™ S9 sepiolite and Aerosil ™ 200 fumed silica are good examples of inorganic stabilizers. The former is able to form a viscous suspension at 3 % (m/m) exhibiting gel-like viscoelasticity and very shear thinning behavior, such that the values of the dynamic viscoelastic functions, the zero-shear viscosity and the apparent yield stress can be tuned by adding either a cationic or an anionic surfactant. Aerosil™ 200 /water dispersions show gel properties at pH 7 from 8 wt% fumed silica. These dispersions can be used as stabilizers even in emulsions with large droplets (>5 microns). 7 wt% fennel oil/W emulsions containing just 4 wt% of Aerosil™ 200 showed an apparent yield point and gel behavior in SAOS.

CONCLUSIONS

This chapter reports on the procedure for the development of ecological emulsions formulated with renewable components as a sustainable alternative to products containing traditional organic solvents. Results obtained with different ecological formulations and emulsification methods are interesting for the applications of green O/W emulsions formulated with several eco-friendly ingredients.

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