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Influence of polysaccharides on the rheology and stabilization of α-pinene emulsions

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ABSTRACT

This work focuses on the need to include polysaccharides in a slightly concentrated O(α-pinene)/W emulsion, formulated with amphiphilic copolymers as emulsifiers. Rheology, laser diffraction and multiple light scattering were the main techniques used to assess the performance of gellan gum, xanthan gum and a mixture of both hydrocolloids as stabilizers. Small amplitude oscillatory shear results were consistent with the existence of three distinct microstructures and relaxation mechanisms, which depended on the hydrocolloid system used. The mechanical spectrum of the emulsion containing both polysaccharides signalled the occurrence of thermodynamic incompatibility between the two. Flow curves fitted to the Carreau–Yasuda model demonstrated a negative synergistic effect between gellan and xanthan gums. The droplet size distribution was similar for these systems, which highlighted the importance of the continuous phase for emulsion stability. Multiple light scattering illustrated that creaming was practically eliminated by the incorporation of polysaccharides, coalescence being the main destabilization mechanism.

1. Introduction

There are many problems in using the conventional agrochemical formulations due to their high concentration of pesticides in formulation, endangering human health and contaminating the environment. Additionally, organic solvents used in the formulations are inflammable and enhance per-cutaneous toxicity by dermal penetration. Legal restrictions introduced by Governments have modified general trends in the development of formulations, which have been directed towards the use of safer solvents in many applications, including agrochemical (Bigorra, 2010; Chu, Liu, & Liu, 2010; ElShafei et al., 2010; Jemâa, Tersim, Toudert, & Khouja, 2012; Merlet, Bigorra, & Ingo, 2010; Moretti, Sanna-Passino, Demontis, & Bazzoni, 2002; Rodilla et al., 2010; Sosa et al., 2012; Varona, Martín, & Cocero, 2009; Varona, Kareth, Martín, & Cocero, 2010).

Hence, suspoemulsions, concentrated emulsions, emulsifiable concentrates, microemulsions and microencapsulated formulations have been developed to fulfil this goal. Such formulations are important in agriculture because less solvent is sometimes possible per unit active ingredient (Mulqueen, 2003). For this purpose, the use of essential oils in O/W emulsions as a tool for pest control has been studied. Among these oils are *Rosmarinus officinalis* and *Myrtus communis* L., which contain high levels of monoterpene hydrocarbons, mainly α-pinene and camphene (bicyclic monoterpene) (Moretti et al., 2002).

α-Pinene is a terpenic solvent. Terpenes are a class of unsaturated hydrocarbons made of isoprene C5 units, which can be derived from essential oils and oleoresins of plants such as conifers. Therefore, they can be classified as renewable solvents and may be interesting alternatives for current volatile organic compounds (VOCs) without requiring changes of equipment or processes (Kerton, 2009). Interestingly, the content of pinene obtained from the essential oil of juniper can exceed 80 wt%. Pinene can be also obtained from the essential oils of rosemary and eucalyptus (Jäger, 2010).

An emulsion O/W, which consists of oil droplets dispersed in an aqueous phase, is a thermodynamically unstable system. Thus, in order to obtain kinetically stable emulsions, their formulation requires the incorporation of substances known as emulsifiers and stabilizers.

Non-ionic or polymeric surfactants are the most effective emulsifiers for this purpose. AB or ABA block copolymers or graft copolymers are the preferred molecular structures within polymeric surfactants, which consist of two groups: the anchor group B, which has a hydrophobic character or, at least, a less markedly hydrophilic character than the other group, known as group A. The latter (group A) forms the main chain. The relationship between the number of A and B groups should be chosen in such a way that maximum adsorption occurs.

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Due to their effectiveness, the use of mixtures of surfactants is recommended for the production of stable emulsions (Mulqueen, 2003). These polymeric surfactants will not only promote the formation of the emulsion but also contribute to its rheological behaviour due to their additional role as a stabilizer, which allows the reduction of the minimum required amount of thickener or stabilizer (Reekmans, 1998). The use of stabilizers in emulsions provokes an increase in viscosity of the continuous phase and as a consequence, improves the long-term physical stability of the emulsion, slowing the movement of the droplets. Clays are used in agrochemical formulations (Aveyard, Binks, & Clint, 2003; Midmore, 1998) and/or polysaccharides such as xanthan gum (Reekmans, 1998). In the case of formulations with polysaccharides, the efficiency depends on the concentration of hydrocolloids in the aqueous phase and of the characteristics of the structure formed by the polymer (McClements, 2005).

Xanthan gum is an anionic high molecular weight extracellular heteropolysaccharide produced from an aerobic fermentation of *Xanthomonas campestri* (Aspinall, 1983; Glicksman, 1969; Graham, 1977; Sworn, 2010). In solution, it gives rise to highly viscous solutions at low concentrations (Sworn, 2010). The use of mixtures of polysaccharides as stabilizers may sometimes be of interest due to the positive synergic effects that may occur. Gellan gum is a polysaccharide rarely used for this type of formulation, despite possessing great practical potential (Sworn, 2009). Gellan gum is an anionic polysaccharide that is produced by microbial fermentation. The native form is highly acetylated. Deacetylation of the macromolecule may be achieved by alkaline treatment to produce a low-acyl gellan gum.

The main aim of this work was to study the influence of the nature of the polysaccharide (low acyl gellan gum, xanthan gum or mixtures of both polymers) on the rheology and physical stability of a model emulsion formulated with a green solvent (α-pinene) and a mixture of amphiphilic emulsifiers of a polymeric nature.

2. Materials and methods

2.1. Materials

Commercial low-acyl gellan gum, Kelcogel F type was used as supplied by CP Kelco Company (San Diego, USA) and xanthan gum was supplied by Sigma Aldrich (batch: 019K0025). The total concentration of polysaccharide in the emulsions was 0.4 wt%.

0.1 wt% sodium azide was added to the final formulation to prevent the growth of microorganisms.

The organic solvent used was rectified α-pinene Leavo 95, an extremely non-polar solvent, which was supplied by Destilaciones Bordas-Chinchurreta Company (Sevilla, Spain). Its density (20 °C) is 898 kg/m^3, its refractive index is 1.464 and its boiling point is around 67.5 °C.

Two types of amphiphilic copolymers were used as emulsifiers, which may be considered to be polymeric surfactants (Martínez, González, Porras, & Gutiérrez, 2005).

Atlas G-5000^{TM} is a hydrophilic AB block (EO-PO) polyalkylene copolymer whose hydrophobic chains, poly-B block of poly (propylene oxide), act as anchoring groups in the organic phase while the hydrophilic chain, poly-A block of poly(ethylene oxide), ensures the stability of the external aqueous phase. The other emulsifier used was Atlox 4913^{TM}, a grafted copolymer of methyl methacrylate and polyethylenglycol. Both surfactants were supplied by Commercial Química Massó Company and are manufactured by Croda.

In addition, a defoaming agent (Dow Corning^{R} MD 10) supplied by Dow Corning was used.

2.2. Methods

2.2.1. Preparation of polysaccharide solutions and preparation of the emulsions

The gum solutions were prepared by slowly dispersing 0.8 wt% gums in deionized water at room temperature. Subsequently, they were mechanically stirred using an IKA-Visc MR-D1 in combination with a Saw-tooth type rotor in a bath at 80 °C in order to facilitate their hydration.

Finally, the water lost due to evaporation during the dispersion and hydration steps was replaced.

Protocol to prepare the emulsion:

1. The components of the aqueous phase (amphiphilic copolymers, and water) were mixed using an Ultra-Turrax T50 (dispersion element G45F) in order to achieve a homogeneous phase.
2. Then α-pinene was added slowly, while the system was agitated using the aforementioned homogenizer (Ultra-Turrax T50).
3. The pre-emulsion was passed through a high-pressure valve homogenizer three times at $14{\cdot}10^4$ kPa (Avestin EmulsiFlex-C5 type).
4. Finally, this emulsion was mixed with an equal amount of a solution of hydrocolloid whose total gum concentration was 0.8%. For this purpose, the Ultra-Turrax T-50 was used. Thus, the EGG30/2/1 emulsion contained 0.4 wt% gellan gum; the EXG30/2/1 emulsion contained 0.4 wt% xanthan gum and the EGGXG30/2/1 emulsion contained 0.2 wt% xanthan gum and 0.2 wt% gellan gum. In the EW30/2/1 emulsion, the amount corresponding to the polysaccharide was replaced by water. In all cases, the emulsions were formulated with 30 wt% α-pinene, 2 wt% Atlas G-5000, 1 wt% Atlox-4913 and 0.05 wt% defoaming agent (MD 10, Dow Corning).

As far as the emulsion formulated without gums (EW30/2/1) is concerned, its rheological characterization could not be carried out since it destabilized rapidly. Thus, the process of destabilization could only be monitored by light multiple scattering technique (MLS).

2.2.2. Oscillatory shear tests

Stress sweeps were performed in a range of 0.05–3 Pa at three different frequencies: 0.1 Hz, 1 Hz and 3 Hz.

Frequency sweep tests (from 3 to 0.01 Hz) were performed by selecting a stress within the linear range.

A controlled-stress rheometer AR2000 with a serrated plate-plate sensor (40 mm diameter, gap: 1 mm) was used. Equilibration time prior to rheological tests was 10 min.

The results obtained provide information on the viscoelasticity of the emulsions studied. The viscoelastic functions used were the storage modulus (G′, related to the elastic component), the loss modulus (G″, related to the viscous response) and the loss tangent (tan δ, which gives the ratio of the viscous over the elastic component). The results shown correspond to emulsions aged for 2 days and represent the mean of four measurements.

2.2.3. Steady shear flow tests

Characterization of the flow behaviour was carried out by using a rheometer from Haake Thermo Scientific (Karlsruhe, Germany) – a Mars controlled stress rheometer with a Vane FL40 sensor system (R_i = 20 mm, R_a = 21,70 mm, H = 55 mm).

All rheological measurements were performed at 20 °C ± 0.1 °C, using a C5P Phoenix circulator (Thermo-Scientific, Germany) for the MARS rheometer and a Peltier system for the AR2000 rheometer for sample temperature control.

The results represent the mean of three measurements done on emulsions aged for 2 days.

2.2.4. Particle size distribution

The mean particle diameter of emulsions aged for two days was calculated from the particle size distribution using a laser diffraction instrument equipped with a 45 mm lens (Mastersizer X, Malvern Instruments, UK). The refraction and absorption indexes used were 1.464 and 1, respectively.

The mean droplet diameters were expressed as Sauter diameter ($D[3,2]$) and volume mean diameter ($D[4,3]$).

$$D[3,2] = \frac{\sum_{i=1}^{N} n_i d_i^3}{\sum_{i=1}^{N} n_i d_i^2}$$

$$D[4,3] = \frac{\sum_{i=1}^{N} n_i d_i^4}{\sum_{i=1}^{N} n_i d_i^3}$$

where d_i is the droplet diameter, N is the total number of droplets and n_i is the number of droplets having a diameter d_i.

The "span" was used to determine the distribution width of droplet sizes, which was calculated as follows:

$$\text{Span} = \frac{D[v,0.9] - D[v,0.1]}{D[v,0.5]}$$

where $D[v,0.9]$ and $D[v,0.1]$ stand for the 90th and 10th percentiles and $D[v,0.5]$ for the median.

2.2.5. Multiple light scattering

Emulsions destabilization was measured by multiple light scattering (Turbiscan Lab Expert) at 20 °C. This technique allows transmitted light (intensity of light that passes through the sample) and backscattered light (intensity of light backscattered by the sample) to be obtained as a function of the sample height.

The results may be presented either as a backscattering percentage (%BS) or in reference mode (delta-backscattering); i.e., by substracting the first scan from all the subsequent scans made.

3. Results and discussion

3.1. Rheological characterization

3.1.1. Dynamic viscoelasticity: small-amplitude oscillatory shear (SAOS)

A small amplitude oscillatory shear test is a technique widely used to determine the viscoelastic behaviour of a system. In order to ensure that the test does not provoke structural damage in the sample, tests should be performed at a stress and strain within the linear viscoelastic range (LVR). Therefore, previous oscillatory torque sweep tests at fixed frequency were conducted in order to estimate the maximum amplitude value of the sinusoidal shear stress function, which guarantees linear viscoelastic behaviour. In a stress sweep, G′ and G″, remain constant up to a critical stress and strain. This is the linear viscoelastic region, where the moduli are independent of the applied stress and strain. Above critical stress, G′ starts to decrease, whereas G″ starts to increase with further increases in critical stress. This is the onset of the non-linear region.

An analysis of the above results establishes a small linear viscoelastic range, whose critical stress varies from 0.13 to 0.25 Pa and whose critical strain amplitude varies from 1.5% to 2.6%.

Mechanical spectra (Fig. 1) show qualitatively different shapes for the three emulsions studied, which reveal different microstructures. The three emulsions display clear viscoelastic properties with a predominance of the elastic component over the viscous component in the frequency range studied. The shape of the spectra

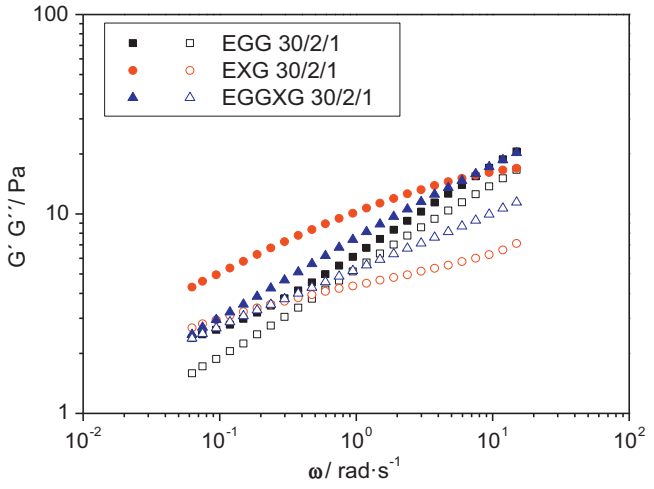

Fig. 1. Mechanical spectra of 30 wt% α-pinene emulsions aged for 2 days as a function of the polysaccharide nature used as stabilizer: gellan gum, EGG30/2/1 (■), xanthan gum, EXG30/2/1 (●) and a 50% mixture of both gums, EGGXG30/2/1 (▲). Temperature: 20 °C. Closed symbols: storage modulus (G′). Open symbols: loss modulus (G″).

corresponding to the plateau zone or "rubbery" zone is the typical behaviour of weak gels. This is consistent with the small linear viscoelastic range shown.

The emulsion stabilized with xanthan gum (XG) shows higher values of the storage modulus (G′) for most of the frequency range studied. This indicates that the aforementioned emulsion is more elastic, as confirmed by the fact that it possesses the lowest values of the loss tangent (viscous component/elastic component) (figure not shown).

The emulsion stabilized with gellan gum (GG) shows G′ values slightly higher than those of G″ at intermediate and higher frequencies. However, the difference between G′ and G″ increases when frequency decreases and the dependence of G′ on frequency become weaker at the lower frequencies studied. This fact is clearly reflected in the loss tangent dependence on the frequency which reveals a crossover of this parameter at lower frequencies of emulsions stabilized with either xanthan gum or gellan gum. The latter shows the lowest values of the loss tangent at low frequencies, which would mean a higher ratio of elastic/viscous components.

The use of gellan gum and xanthan gum in identical percentages does not lead to a positive synergistic effect on the mechanical spectrum. This means that the resulting emulsion does not show more marked elastic properties. G′ values are intermediate between those shown in the emulsions stabilized with XG and those shown in the emulsions stabilized with GG at the intermediate frequencies studied. However, it should be emphasized that the G′ values of the emulsion containing both gums are coincident with those of the emulsion with GG at higher frequencies (that is, they show the same dependence on frequency). This means that gellan gum is responsible for the elastic response at higher frequencies for the emulsion containing both gums. In addition, the values of G″ for the emulsion stabilized by both gums are intermediate between those corresponding to the emulsions that contain just one gum at intermediate and high frequencies. Notably, the values of G″ are very similar to those of the XG-stabilized emulsion and very different to those of the emulsion stabilized with GG at lower frequencies. This suggests that XG dominates the viscous response of the emulsion at lower frequencies (at longer relaxation times). The results obtained are consistent with those reported by Rodríguez-Hernández and Tecante on a study of mixed gels of xanthan and gellan (1999).

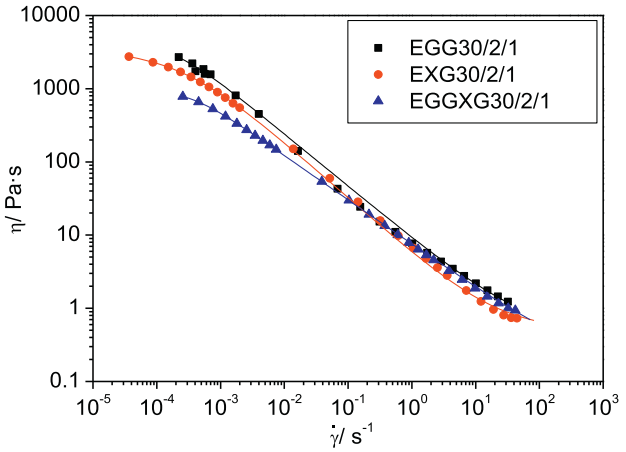

Fig. 2. Steady shear flow curves of 30 wt% α-pinene emulsions aged for 2 days as a function of the polysaccharide nature used as stabilizer: gellan gum, EGG30/2/1 (■), xanthan gum, EXG30/2/1 (●) and a 50% mixture of both gums, EGGXG30/2/1 (▲). Temperature: 20 °C. Continuous lines illustrate data fitting to the Carreau–Yasuda model.

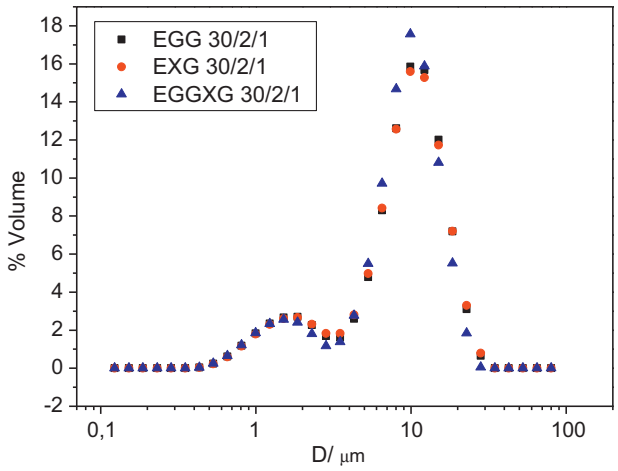

Fig. 3. Droplet size distribution of 30 wt% α-pinene emulsions aged for 2 days as a function of the polysaccharide nature used as stabilizer: gellan gum, EGG30/2/1 (■), xanthan gum, EXG30/2/1 (●) and a 50% mixture of both gums, EGGXG30/2/1 (▲). Temperature: 20 °C.

The above results show that the stabilizing action of both gums is independent. This fact is consistent with the existence of thermodynamic incompatibility between gellan and xanthan gums (Zasypkin, Braudo, & Tolstoguzov, 1997). In other instances, this may lead to substantial enhancements in gel strength and provoke an increase of the effective concentration of both polymers, by confining them to only part of the total volume due to segregation interactions (Harrington & Morris, 2009).

When two different polysaccharide solutions are mixed, enthalpic interactions between chains of different types may be more favourable (associative interactions) or less favourable (segregative interactions) than interactions between chains of the same type (Piculell et al., 1994). Segregative interactions, also known as "thermodynamic incompatibility", are more common, and sufficiently high concentrations of the two polymers can lead to spontaneous system separation into two coexisting liquid phases (Grinberg, Ya, & Tolstoguzov, (1997); Piculell, Bergfeldt, & Nilsson, 1995; Zasypkin et al., 1997).

3.1.2. Flow curves

Fig. 2 shows the apparent viscosity as a function of the shear rate for the emulsions studied. The apparent viscosity values represent the mean of three measurements.

Emulsions formulated with one polysaccharide and those formulated with the mixture of both polysaccharides show flow curves with three different zones: (a) at lower shear rate, the apparent viscosity tends to reach a Newtonian plateau where the viscosity is independent of shear rate (zero shear viscosity, η_0), (b) at intermediate shear rates, shear thinning behaviour is observed, which is characterized by a decrease in the apparent viscosity with increasing shear rate, and (c) emulsions exhibit a similar trend to reach a Newtonian plateau at higher shear rates (infinite shear viscosity, η_∞).

The above-described behaviour has been fitted to the Carreau–Yasuda model (Yasuda, Armstrong, & Cohen, 1981). In Fig. 2, continuous lines illustrate data fitting to the Carreau–Yasuda model.

$$\eta = \eta_\infty + \left[\frac{\eta_0 - \eta_\infty}{1 + (\dot{\gamma}/\dot{\gamma}_c)^p}\right]^{(1-n)/p}$$

where η_0 stands for zero shear viscosity, η_∞ stands for infinite shear viscosity, $\dot{\gamma}_c$ is critical shear rate associated with the onset of structural collapse, p is a fitting parameter, and n is the flow index.

An analysis of the parameters (Table 1) reveals that the polysaccharide used has an influence on the zero shear viscosity and on the slope of the shear-thinning zone. The emulsion formulated with gellan gum shows a higher value of η_0 than that shown by the emulsion with xanthan gum. Furthermore, the use of the mixture of both gum solutions in the emulsion provokes a negative synergistic effect. Conversely, positive synergistic effects are known to occur between xanthan gum and galactomannans (guar, locust bean, LBG) (López-Munguía et al., 2004; Lundin & Hermansson, 1995; Mannion et al., 1992; Tako & Nakamura, 1985; Zhan, Ridout, Brownsey, & Morris, 1993). They are also very common in starch–hydrocolloid mixtures (BeMiller, 2011).

It is interesting to note that the emulsion EGG, stabilized with gellan gum held the Cox–Merz rule (data not shown), conversely to emulsions formulated with xanthan gum or the mixture of both gums. This fact highlights the role of gellan gum, a polysaccharide currently used to form either strong gels (Sworn, 2009) or fluid gels (García, Alfaro, Calero, & Muñoz, 2011), as a gum able to provide α-pinene emulsions with enhanced resistance against structural breakdown under shear.

Table 1 also shows that the critical shear rate, which indicates the behaviour change from Newtonian to shear thinning, varies conversely with the zero-shear viscosity. The flow index values indicate that the most and the least shear thinning emulsions are those stabilized by xanthan and the mixture of both gums, respectively. It must be emphasized that the emulsion formulated with both gums shows the lowest zero-shear viscosity, the highest critical shear rate, and the lowest shear thinning character, which is associated with a weak microstructure.

3.2. Droplet size distribution

Fig. 3 shows the droplet-size distribution expressed as volume distribution for all emulsions studied after an ageing time of 2 days. It is noted that the three emulsions show the same droplet size distribution regardless of the polysaccharide used as stabilizer. In fact, Sauter mean diameter as the volume mean diameter and span (Table 2) show no significant differences for all emulsions studied (taking into account standard deviations). This indicates the initial droplet size distribution was controlled by the rotor-stator

Table 1
Influence of the polysaccharide nature used as stabilizer of 30 wt% α-pinene emulsions aged for 2 days on the fitting parameters of the Carreau–Yasuda equation for flow curves at 20 °C.

	η_∞ (Pa s)	η_0 (Pa s)	SD η_0	$\dot{\gamma}_c$ (s^{-1})	SD $\dot{\gamma}_c$	p	SD p	n	SD n	R^2
EGG 30/2/1	0.5	4506	802	1.7×10^{-4}	8×10^{-5}	1.20	–	0.29	0.07	0.992
EXG 30/2/1	0.4	3403	36.2	2.4×10^{-4}	1×10^{-5}	0.75	0.02	0.24	0.05	0.999
EGGXG30/2/1	0.5	1144	80.6	3.3×10^{-4}	2×10^{-6}	0.99	0.13	0.36	0.11	0.999

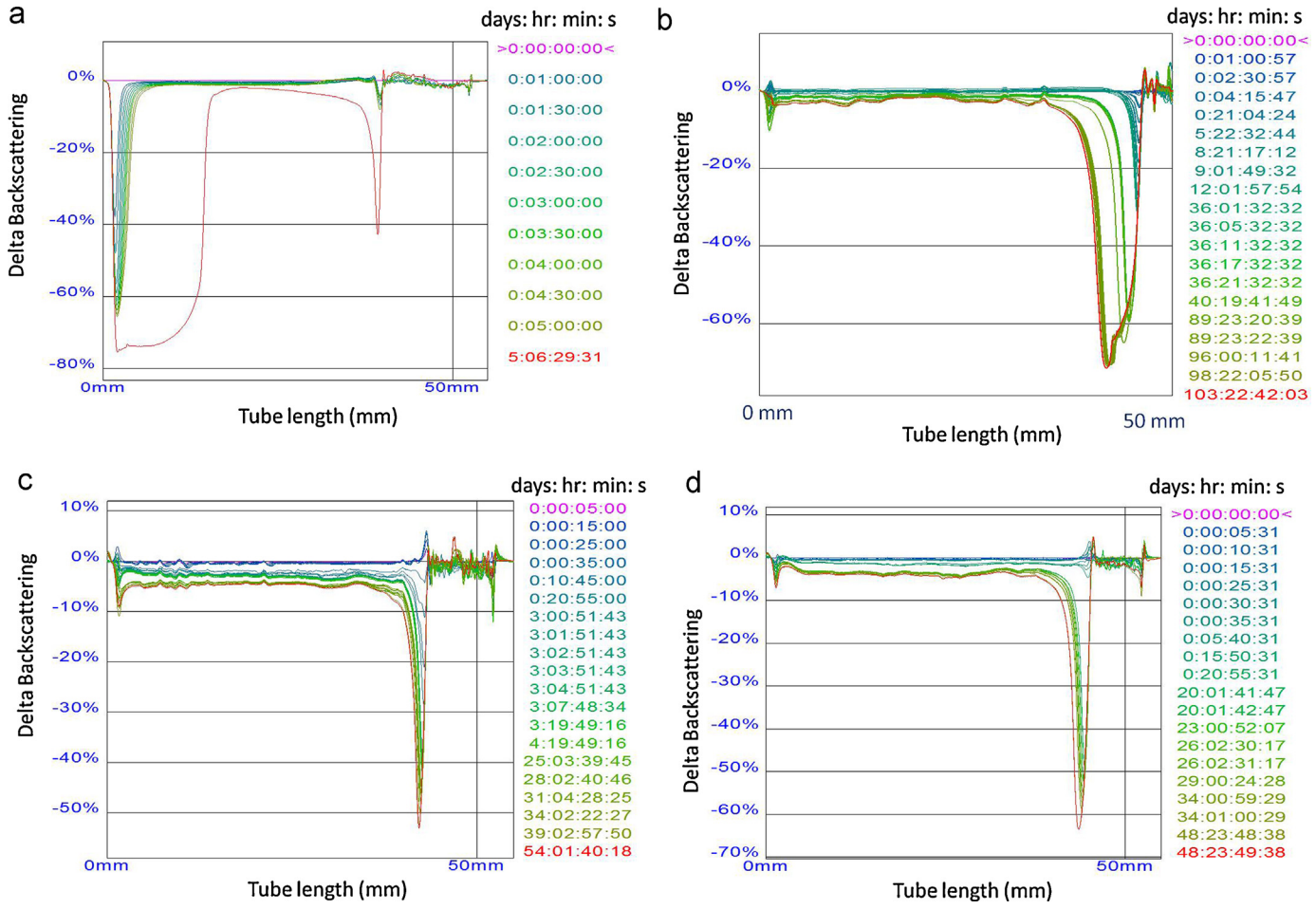

Fig. 4. Changes in delta backscattering profiles as a function of the tube length with the storage time in quiescent conditions for 30 wt% α-pinene emulsions prepared with: (a) without gum, (b) gellan gum, (c) xanthan gum, (d) a 50% mixture of both gums. Tube length: 55 mm, temperature: 20 °C.

followed by the high-pressure valve homogenizer and that the effect of the final mixing step with the aqueous gum dispersion was negligible. Distributions were non-Gaussian curves and indicated that two populations were present. This fact indicates that the differences found in mechanical spectra cannot be attributed to changes in their droplets size distributions. Thus, the microstructural changes supported by SAOS may be attributed to the different nature of the structural network formed by gellan gum, xanthan gum and the mixture of both gums in the continuous phase of the emulsion.

3.3. Physical stability study by multiple light scattering

The physical stability of the emulsions was studied by the MLS technique in order to detect incipient destabilization phenomena before they may be detected by visual observation. Fig. 4 shows the backscattering profiles in the reference mode of the emulsions studied.

Fig. 4a shows a decrease of delta-backscattering function with ageing time for the emulsion formulated in the absence of polysaccharides. This effect is observed along the full length of the cell

Table 2
Influence of the polysaccharide nature used as stabilizer of 30 wt% α-pinene emulsions aged for 2 days on the Sauter ($D[3,2]$) and volumetric ($D[4,3]$) mean diameters and the span.

	$D[3,2]$ μm	SD $D[3,2]$	$D[4,3]$ μm	SD $D[3,2]$	Span	SD span
EGG30/2/1	4.38	0.09	8.78	0.07	1.60	0.02
EXG30/2/1	4.41	0.11	8.78	0.13	1.63	0.01
EGGXG30/2/1	4.38	0.05	8.34	0.11	1.52	0.04

Table 3
Fitting parameters of first-order kinetic equation for the BS% in the 19.8–20 mm zone of the tube versus ageing time for 30 wt% α-pinene emulsions, at 20 °C, as a function of polysaccharide nature used as stabilizer.

	BS_e	SD_{BSe}	$BS_0 - BS_e$	SD_{BS_0-BSe}	$K\,(s^{-1})$	R^2
EGG30/2/1	76.1	0.03	2.1	0.1	$1.69\,e^{-07}$	0.991
EXG30/2/1	74.0	0.03	4.0	0.1	$4.00\,e^{-06}$	0.990
EGGXG30/2/1	75.9	0.07	3.2	0.1	$1.00\,e^{-05}$	0.977

containing the sample, being more marked at the bottom of the container. At the bottom of the cell, a backscattering drop became particularly pronounced with the passage of time. This fact may be explained by a migration of solvent droplets from the bottom of the vial to higher zones. This provokes a decrease of droplet concentration at the bottom of the cell (clarification) (Mengual, Meunier, Cayre, Puech, & Snabre, 1999), which indicates a destabilization process by creaming. Furthermore, the clear decrease of delta backscattering at the top of the cell indicates a further destabilization process by coalescence, which is less significant than the creaming phenomenon. The occurrence of the creaming process could be detected by visual inspection after 5 days time. However, no phase separation as a result of coalescence was observed in the upper part of the cell. The results obtained demonstrated that the MLS technique is a powerful tool in predicting destabilization processes, due to its ability to detect the onset of the creaming phenomenon after just one hour's time.

The effect of the incorporation of gellan gum, xanthan gum or a mixture of both on the stability of emulsions was analyzed in the following figures.

Fig. 4b also shows the results obtained in reference mode for the emulsion stabilized by gellan gum. In this case, the emergence of a destabilization process by creaming was not observed. However, a slow decrease in the delta-backscattering function in the central part of the cell was detected, which can be attributed to the onset of coalescence. The absence of an isobestic point indicates an increase in droplet size in accordance with the multiple light scattering theory, which postulates that at sizes greater than 0.6 μm, a decrease in backscattering with increasing particle size is produced (Mengual et al., 1999).

The changes in delta-backscattering in the upper zone of the cell are due to a decrease in the volume of the sample in the measurement zone; therefore they should not be associated with any destabilization mechanism. This decrease of the sample volume could be due to a structure compaction by a mechanism similar to that described for concentrated aqueous suspensions (Faers & Kneebone, 1999; Faers, Choudhury, Lau, McAllister, & Luckham, 2006). This mechanism was described by Michael and Bolger (1962) in terms of compression in order to describe the flocculation volume and flocculation rate for kaolin suspensions.

The occurrence of a slow coalescence process led to a clear phase separation at the top of the cell after a prolonged ageing time.

Fig. 4c and d indicate that the emulsion with xanthan gum and that with the mixture of both gums underwent the same type of destabilization mechanism as that described for the emulsion containing gellan gum.

Further information on the influence of the hydrocolloid on the stability of the emulsion was provided by a kinetic study (variation of backscattering with ageing time). To be more precise, the average value of the backscattering (BS) measurement at the central zone of the cell (between 19.8 and 20 mm of sample height) has been plotted as a function of ageing time (Fig. 5). The progressive fall of BS% is noticeable (related to droplet size increase) with ageing time for the emulsion stabilized with gellan gum. Additionally, this slope is much steeper for the other two cases.

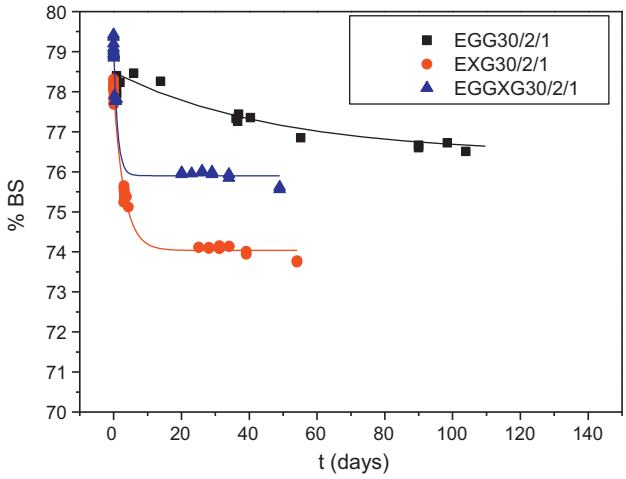

Fig. 5. Variation in backscattering (BS%) in the 19.8–20 mm zone monitored over 50 days, for a sample stored in quiescent conditions at 20 °C. The destabilization kinetics correspond to 30 wt% α-pinene emulsions stabilized with gellan gum, EGG30/2/1 (■), xanthan gum, EXG30/2/1 (●) or a 50% mixture of both polysaccharides, EGGXG30/2/1 (▲). Measuring cell length: 55 mm. Continuous lines show BS% values predicted by the first-order kinetic model used.

The results shown in Fig. 5 were fitted to an exponential equation, typically used for a first-order kinetic model.

$$BS = BS_e + (BS_0 - BS_e)\exp(-K \cdot t)$$

where BS stands for backscattering as a function of ageing time, BS_e is the corresponding equilibrium value, BS_0 is the initial value of backscattering, K is the first-order kinetic coefficient.

An analysis of the fitting parameters (Table 3) shows that the gellan gum stabilized emulsion possessed the lowest kinetic coefficient of the destabilization process. This indicates that the use of this polysaccharide provided an improvement in the physical stability of the emulsion in comparison with the use of xanthan gum or the mixture of both. This result is consistent with the fact that the emulsion stabilized with gellan gum exhibited the highest "zero-shear viscosity". The emulsion containing the mixture of both gums showed the highest value of K, which leads to the fastest kinetic destabilization. This is consistent with the fact that this emulsion showed the lowest zero-shear viscosity value. The results obtained in this study indicate that the lack of positive synergy and the occurrence of thermodynamic incompatibility between the xanthan gum and gellan gum have a negative effect on their role as a stabilizer for this type of emulsion.

4. Conclusions

The preparation protocol for the emulsions used in this study leads to bimodal droplet size distributions regardless of the hydrocolloid used.

The linear viscoelastic properties of the slightly concentrated α-pinene emulsions formulated with a mixture of copolymers as emulsifier depends strongly on the hydrocolloids used as stabilizers and elastic properties dominate over viscous properties.

Mechanical spectra show that gellan gum controlled the relaxation process at shorter times, whereas xanthan gum controlled it at longer times. This fact supports the occurrence of thermodynamic incompatibility between both gums in the continuous phase of the emulsions.

Flow curves of the emulsions studied have been fitted to the Carreau–Yasuda model. The fitting parameters values depend on the hydrocolloids used. The gellan gum stabilized emulsion exhibits a strong shear thinning character, the lowest critical shear rate for the onset of non-Newtonian response and the highest value of zero-shear viscosity. In contrast, the zero shear viscosity is lowest for the emulsion stabilized by the mixture of gellan and xanthan gums, which indicates a negative synergetic effect.

The multiple light scattering technique demonstrates the advantages of including a hydrocolloid as the stabilizer in the formulation. The addition of gellan gum, xanthan gum, or a mixture of both eliminates creaming. It has also been shown that these emulsions undergo a slow coalescence process, whose kinetic model corresponds to a first-order kinetic process. This allows the BS% dependence on ageing time to be fitted to a single exponential equation. The gellan gum stabilized emulsion shows the slowest kinetics of destabilization, which is consistent with its higher value of zero-shear viscosity.

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