

Rheology of oleogels based on sorbitan and glyceryl monostearates and vegetable oils for lubricating applications

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RESUMEN

Reología de oleogeles basados en monoestearatos de sorbitano y glicerilo y aceites vegetales para aplicaciones lubricantes.

En el presente trabajo se han estudiado diferentes oleogeles, basados en monoestearatos de sorbitano y glicerilo y aceites vegetales, que podrían ser potencialmente empleados como alternativas biodegradables a las grasas lubricantes tradicionales. En concreto, se ha evaluado su comportamiento reológico, a través de ensayos en cizalla oscilatoria, y algunas propiedades relacionadas con su rendimiento en la lubricación, tales como su estabilidad mecánica y comportamiento tribológico. La respuesta reológica y la estabilidad mecánica de los oleogeles estudiados están significativamente influenciadas por el tipo y la concentración del agente gelificante y por el aceite vegetal empleado. Así, el monoestearato de glicerilo (GMS) produce, generalmente, geles más fuertes que el monoestearato de sorbitano (SMS). El uso de aceites de baja viscosidad, como los aceites de colza o de soja, dan lugar a geles con valores más altos de las funciones viscoelásticas lineales que los oleogeles preparados con aceite de ricino. El comportamiento reológico de los oleogeles de SMS depende, además, de la velocidad de enfriamiento durante la gelificación. Por otra parte, los oleogeles estudiados presentan bajos valores del coeficiente de fricción, determinado en un contacto tribológico, aunque sólo algunos oleogeles que contienen GMS y aceite de ricino muestran una estabilidad mecánica adecuada.

PALABRAS CLAVE: Aceites vegetales – Bio-lubricantes – Oleogeles – Reología.

SUMMARY

Rheology of oleogels based on sorbitan and glyceryl monostearates and vegetable oils for lubricating applications.

Oleogels based on sorbitan and glyceryl monostearates and different types of vegetable oils, potentially applicable as biodegradable alternatives to traditional lubricating greases, have been studied. In particular, the rheological behavior, by means of small-amplitude oscillatory shear (SAOS) measurements, and some lubrication performance-related properties (mechanical stability and tribological response) have been evaluated in this work. SAOS response and

mechanical stability of these oleogels are significantly influenced by the type and concentration of the organogelator and the vegetable oil used in the formulations. Glyceryl monostearate (GMS) generally produces stronger gels than sorbitan monostearate (SMS). The use of low-viscosity oils, such as rapeseed and soybean oils, yields gels with significantly higher values of the linear viscoelastic functions than oleogels prepared with high-viscosity oils, i.e. castor oil. The rheological behavior of SMS-based oleogels also depends on the cooling rate applied during the gelification process. On the other hand, the oleogels studied present low values of the friction coefficient obtained in a tribological contact, although only some GMS/castor oil-based oleogels exhibit a suitable mechanical stability.

KEY-WORDS: Bio-lubricants – Oleogels – Rheology – Vegetable oils.

1. INTRODUCTION

Oleogels, also referred to as organogels or lipogels, are semisolid materials composed of an amphiphilic molecule, usually known as organogelator, and a hydrophobic liquid. The microstructure of oleogels is characterized by either permanent rigid networks or transient semiflexible meshes, both thermoreversible. Examples of oleogels are those containing, for instance, ethylcellulose, cholesterol, sorbitan monostearate or lanolin alcohols, as organogelators, dispersed in vegetable oils, as organic solvents (Almeida and Bahia, 2005). Different oleogel applications have been investigated over the past few years. It is worth mentioning their potential use in the area of environmental chemistry, and in the pharmaceutical and cosmetic industries (Hinze *et al.*, 1996), sometimes related to the discovery of new gel-forming molecules in organic solvents. These hydrophobic gel materials do not require new nor extensive manufacturing knowledge in order to be produced, and can be formulated in a wide viscosity range (Almeida and Bahia, 2006).

Up to now, oleogels have not been widely explored for lubricating applications. However, it is obvious that the lubricant industry and its customers

are interested in new products that do not diminish the finite world resources of mineral hydrocarbons and, on the other hand, have a minimal adverse impact on the environment. Inside the field of lubricants, oleochemicals are the natural alternative to mineral oils (Adhvaryu and Erhan, 2002). It is worth remembering that fatty acid-based products from vegetable and animal origins were used as lubricants in the past until mineral oils began to become available in large volumes with competitive prices. However, every year, worldwide, millions of tonnes of engine, industrial and hydraulic oils leak into the ground or waterways or are disposed of in the environment, with the well-known adverse effect on aquatic life. In order to minimize the contamination damage that petroleum-based products cause in the environment, there has been an increasing demand for environmentally acceptable products suitable for use as lubricants (Wilson, 1998). In this sense, a slow, but steady, movement toward the use of "environmentally friendly" or more readily biodegradable lubricants has been promoted during the last decade.

Erhan and co-workers (Erhan and Asadauskas, 2000; Adhvaryu and Erhan, 2002; Adhvaryu *et al.*, 2004; Erhan *et al.*, 2006) have reported some advantages and disadvantages concerning the use of vegetable oils and organic esters as liquid lubricants. As they pointed out, the main disadvantage of vegetable oils is their poor oxidative stability in comparison to some of the mineral oils traditionally employed. However, they present good lubricity and ability to adhere to metal surfaces, low volatility, small viscosity-temperature dependence and, of course, non-toxicity and high biodegradability. Some solutions for overcoming the problems related to the low viscosity of vegetable oils for different lubricating applications have also been previously reported (Quinchia *et al.*, 2009; Garcia-Zapateiro *et al.*, 2010). Nevertheless, the development of environmentally friendly lubricating grease formulations, based on 100% biodegradable raw materials, seems to be a much more difficult task. Greases may be considered gel-like colloidal suspensions in which

a suitable thickener, generally a metallic soap, is dispersed in a lubricating liquid, traditionally a mineral or synthetic oil (NLGI, 1994). The replacement of the base oil with a biodegradable material is possible using vegetable oils, as previously mentioned. However, the use of a "green thickener", able to replace metallic soaps and yield a formulation with the proper characteristics for use as a lubricating grease, is not a completely solved problem at present. In this framework, some rheological and technological (related to their performance as lubricants) properties of several oleogels, containing sorbitan and glyceryl monostearates as organogelators and different types of vegetable oils, have been studied and related to their potential use as biodegradable alternatives to traditional lubricating greases.

2. MATERIALS AND METHODS

2.1. Materials

Castor oil, purchased from Guinama (Spain), and rapeseed and soybean oils, kindly supplied by Fresenius-Kabi Deutschland GmbH, were used to prepare oleogel formulations. The fatty acid compositions and kinematic viscosity values at 40°C of the different vegetable oils are listed in Table 1. The sorbitan monostearate (SMS) of HLB = 4.7 and the glyceryl monostearate (GMS) of HLB = 4.2, from Panreac and Guinama respectively, were used as gelling agents. Some standard lithium 12-hydroxystearate lubricating greases were used as reference systems. They were prepared, as described elsewhere (Franco *et al.*, 2005; Delgado *et al.*, 2005), using 12-hydroxystearic acid, hydrated lithium hydroxide, and paraffinic and naphthenic mineral oils, all of them supplied by Verkol Lubricantes S. A. (Spain).

2.2. Oleogel preparation

The processing of oleogels was performed in an open vessel, using an anchor impeller (D = 90 mm;

Table 1
Fatty acid compositions and kinematic viscosities of the vegetable oil samples used in this study

	Castor oil	Rapessed oil	Soybean oil
Kinematic viscosity at 40 °C (cSt)	211	36	33
Fatty acid composition (%):			
Palmitic acid (C16:0)	2.6	4.6	10.7
Stearic acid (C18:0)	2.7	–	3.4
Oleic acid (C18:1)	6.3	66.0	24.1
Linoleic acid (C18:2)	10.8	21.1	54.7
Linolenic acid (C18:3)	–	8.2	6.0
Ricinoleic acid (12OH-C18:1)	77.6	–	–

H = 110 mm) to disperse the gelling agent. Batches of 600 g were prepared, employing SMS and GMS concentrations between 10 and 20% w/w. SMS and GMS were dispersed in the vegetable oil under agitation (60 rpm), for 60 min, at around 60°C, a temperature slightly higher than their melting points in order to favor dispersion. Afterwards, the solution was cooled to room temperature to induce gelification. Cooling was carried out either by natural convection, switching off the thermostatic device, or placing the vessel into a large quenching system of water at 0°C under mild agitation.

2.3. Gas chromatography

Gas chromatography analysis was performed with an Agilent 6890 chromatograph equipped with a flame-ionization detector in order to determine the fatty acid profiles in the vegetable oils studied. C14-C24 FAMES provided standards were used.

2.4. Oil viscosity measurements

Oil dynamic viscosity data were determined at 40°C. Viscous flow tests were carried out in a rotational controlled-strain ARES rheometer (Rheometrics Scientific, UK), using a coaxial cylinder geometry (inner diameter: 32 mm, outer diameter: 34 mm, cylinder length: 33.35 mm). The shear rate range applied was comprized between 5 and 500 s⁻¹. All the samples showed Newtonian behavior. Kinematic viscosity was then calculated as the ratio of the dynamic viscosity to the density. Density measurements were performed at 40°C in a capillary densimeter, model DMA-5000 (Anton Paar, Austria).

2.5. Oleogel rheological characterization

The rheological characterization of oleogels was performed in both controlled-stress (Rheoscope, ThermoHaake, Germany) and controlled-strain (ARES, Rheometric Scientific, UK) rheometers, in a temperature range of -10 and 50°C. Small amplitude oscillatory shear (SAOS) tests, inside the linear viscoelasticity regime, were carried out in a frequency range of 0.01 and 100 rad/s. A profiled plate-and-plate geometry (25 mm diameter, 1 mm gap and 0.4 relative roughness) was used. Stress or strain sweep tests, at the frequency of 1 Hz, were previously carried out on each sample to determine the linear viscoelasticity region. A bath heating unit fitted to the static plate of the tool and a convection oven that encloses the sample were used to control the temperature in the controlled-stress and controlled-strain rheometers, respectively. At least two replicates of each test were carried out on fresh samples.

2.6. Penetration and mechanical stability tests

Both unworked and worked penetrations were determined using a Seta Universal penetrometer,

model 17000-2, with one-quarter cone geometry (Stanhope-Seta, UK). The one-quarter scale penetration values were converted into the equivalent full-scale cone penetration values, according to the ASTM D 217 standard. Classic consistency NLGI grade was established according to these penetration values (NLGI, 1994). Samples were tested for 30 minutes in a Roll Stability Tester, model 19400-3 (Stanhope-Seta, UK), and penetration measurements were carried out, once again, immediately after the rolling test and again after 5 hours, in order to evaluate their mechanical stability and consistency recovery.

2.7. Measurements of the friction coefficient

A classic ball-disc tribometer was used to determine the friction coefficient, which is defined as the relationship between the applied load (normal force) and the friction force, under flooded flow lubrication, i.e. under the assumption that the lubricant is supplied to the film inlet at a sufficient flow rate. Original bearing balls made of 100Cr6 (12.7 mm diameter) were employed, all of them with the same roughness and hardness. Steel plates were made of 9SMn28. In this device, the plate rotated while the ball was kept fixed. The lubricant was spread homogeneously onto the steel plate, and the ball was supported by a holder on the sample. This arm was also put into contact with a force sensor, which directly measured the friction force. The friction force was measured, for 900 s, at room temperature (25 ± 1°C). This test was repeated three times, to obtain an accurate average friction factor. Taking into account sampling and measurement errors, the friction factor values had an average standard deviation of ± 0.01. For each test, a new contact area on the ball surface was used and all surfaces were cleaned with ethanol.

3. RESULTS

3.1. Linear viscoelasticity

a) Influence of processing thermal protocol

It is well-known that the manufacturing process of standard lithium soap-based lubricating greases is highly complex, with many thermo-mechanical variables affecting the final properties of this gel-like dispersion, i.e. rheological behavior and mechanical stability among others (Delgado *et al.*, 2005; Franco *et al.*, 2005). On the other hand, it has been reported that the mechanism of gelification in aqueous systems is highly affected by the thermal protocol selected (Nunes *et al.*, 2006; Zhong *et al.*, 2004). In the case of SMS/castor oil gels (see Sanchez, *et al.*, 2008), the rheological behavior is influenced by the thermo-mechanical protocol selected to induce gelification, and, especially, by the cooling profile. This effect is

clearly illustrated in Figure 1a, where the SAOS functions, storage (G') and loss (G'') moduli, are plotted against frequency. As can be observed, differences of around one decade are found in the values of both viscoelastic functions for SMS-based oleogels cooled under natural convection mechanism (room temperature, around 25°C) or in water at 0°C. On the contrary, the cooling profile applied during gelification does not significantly affect the rheological response of GMS-based oleogels, as can be seen in Figure 1b. Only a slight increase in the relative elastic characteristics of the sample is noticed by cooling the incipient oleogel in water at 0°C. Thus, the influence of the thermo-mechanical processing protocol is a distinctive variable to take into account in both types of organogelators studied.

b) Influence of gelling agent concentration

Figure 2 shows the influence of the gelling agent concentration on SAOS response of both SMS/castor oil and GMS/castor oil gels. As expected, the values of G' and G'' always increase with gelling agent concentration, more dramatically in the case of SMS-based gels. In addition, some qualitative differences in the rheological behavior can be also observed. Thus, in the case of GMS-based oleogels, G' is always larger than G'' in the whole frequency range studied, and a well-developed plateau region in the mechanical spectrum is

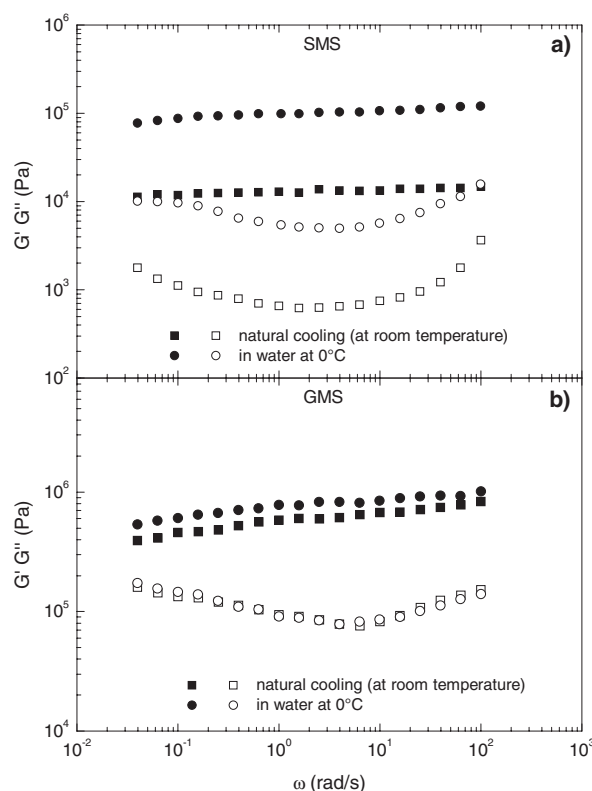


Figure 1
Frequency dependence of the storage and loss moduli, at 25°C, for a) SMS/castor oil, and b) GMS/castor oil oleogels processed under different cooling profiles (G' full symbols, G'' open symbols; organogelator concentration: 20% w/w).

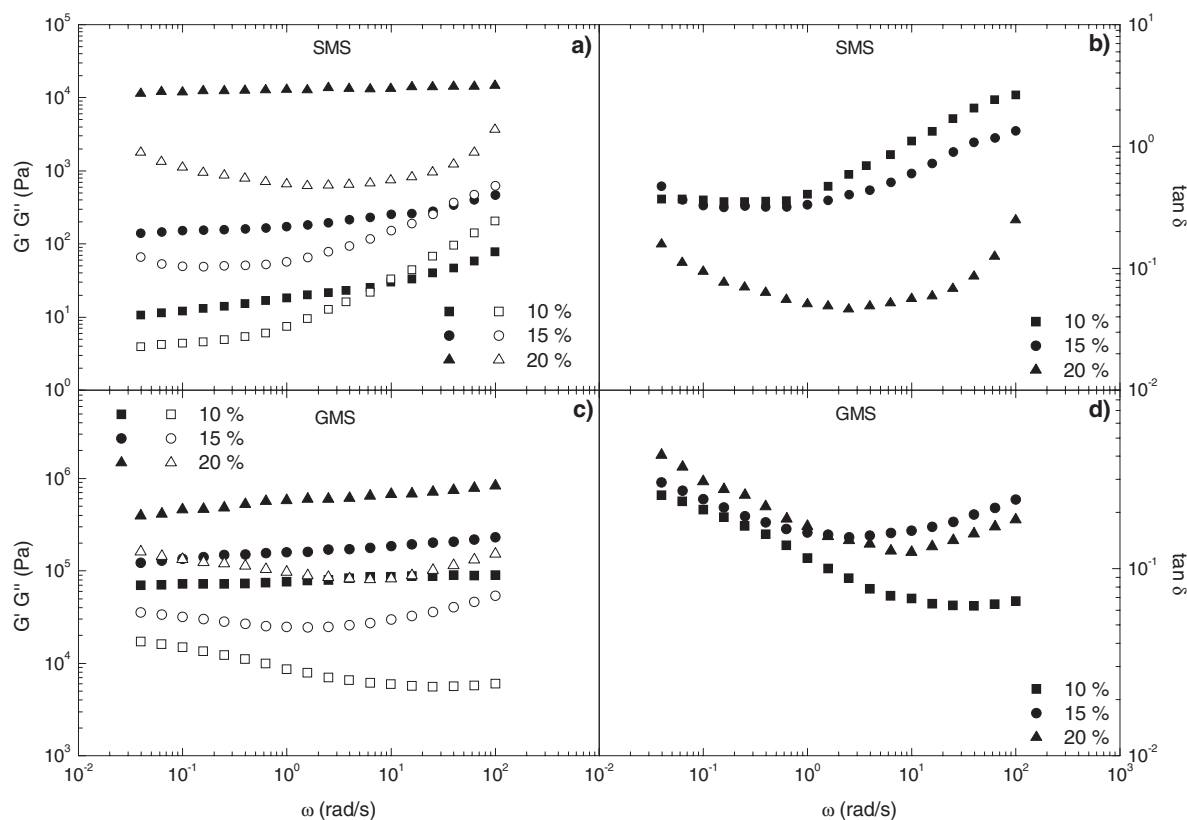


Figure 2
Frequency dependence of (a, c) the storage and loss moduli, and (b, d) the loss tangent, at 25°C, for oleogels prepared with different SMS and GMS concentrations (G' full symbols, G'' open symbols).

noticed, i.e. an apparent minimum in G'' and a power-law relationship for G' with slopes of around 0.1-0.2. This behavior is typical of entangled polymers (Ferry, 1980) and gel-like disperse systems (Mewis and Spaull, 1976; Franco *et al.*, 1995; Gallegos *et al.*, 2004; Ruiz-Márquez *et al.*, 2010), including standard lubricating greases (Delgado *et al.*, 2006a; Martín-Alfonso *et al.*, 2007, 2009). This minimum in G'' is shifted to high frequencies for the lowest GMS concentration, yielding slightly lower values of the loss tangent ($\tan \delta = G''/G'$) (Figure 2d). On the contrary, for SMS-based oleogels, an extensive plateau region is only apparent for the oleogel containing the highest SMS concentration evaluated (20% w/w). At lower concentrations, a crossover between both SAOS functions (which is shifted to lower frequencies as SMS concentration decreases), and similar values for both linear viscoelasticity functions, indicative of weak gels (Lizaso *et al.*, 1999; Heng *et al.*, 2005), are observed (Figure 2a). As a consequence, relatively high values of the loss tangent are obtained for 10% and 15% w/w SMS concentrations (Figure 2b).

c) Influence of temperature

Figure 3 shows the evolution of SAOS functions with frequency, as a function of temperature, for selected SMS- and GMS-based oleogels. No linear viscoelasticity range was detected at temperatures higher than those indicated in Figure 3, as a consequence of the proximity to the sol-gel transition (55-60°C). As can be expected, the values of both SAOS functions generally decrease with temperature. In addition, an evolution from the plateau to the terminal region of the mechanical spectrum can be noticed at the highest temperatures, mainly for SMS-based oleogels. On the other hand, the frequency dependence of both moduli is not highly influenced by temperature for GMS-based oleogels thus exhibiting a well-developed plateau region even at high temperatures. Moreover, the values of SAOS viscoelastic functions are almost identical up to around 35°C and then decrease with temperature. More surprisingly, the loss tangent is not greatly affected (data not shown), which indicates that the relative elastic characteristics of the oleogels are not influenced by temperature either.

As previously reported for standard and biodegradable greases (Delgado *et al.*, 2006b, Sánchez *et al.*, 2008, 2011), the plateau modulus, the characteristic viscoelastic parameter associated to the plateau region (Ferry, 1980), can be used to quantify the influence of temperature on the linear viscoelastic properties of these oleogels. An Arrhenius-type equation fits the evolution of this viscoelastic parameter with temperature fairly well:

$$G_N^0 = A \cdot e^{\frac{E_a}{R} \cdot \left(\frac{1}{T}\right)} \quad (1)$$

where E_a is a parameter that evaluates oleogel thermal susceptibility, similar to the activation energy

(J/mol), R is the gas constant (8.314 J/mol K), T is the absolute temperature (K), and A is the pre-exponential factor (Pa).

Once again, as may be deduced from the previous discussion, different behavior was found depending on the type of thickener used. In the case of the SMS-based oleogel, equation (1) fits the G_N^0 values, in the whole temperature range studied, fairly well, as can be observed in Figure 4. This behavior, in a much wider temperature range, was observed in biodegradable greases manufactured with castor oil and cellulosic derivatives (Sánchez *et al.*, 2008, 2011). On the contrary, two different Arrhenius-type equations are necessary to fit the evolution of the GMS-based oleogel. Thus, the thermal susceptibility of this oleogel is very low (SAOS viscoelastic function values almost constant) below a critical temperature, while oleogel thermal susceptibility is much more dramatic above it. This last behavior is quite similar to that shown by standard lithium lubricating greases (Delgado *et al.*, 2006b). In this sense, the E_a value (Figure 4) found for the GMS-based gel in the low-temperature range is similar to those obtained for lithium lubricating greases up to around 110°C. Above this temperature, the thermal dependence of lithium greases is more similar to that shown by the SMS-based oleogel. Evidently, in

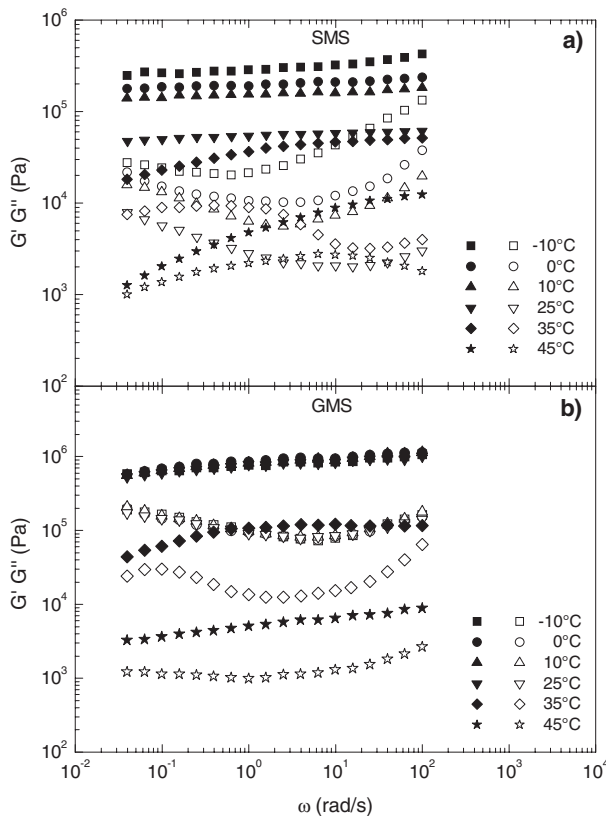


Figure 3 Frequency dependence of the storage and loss moduli, at different temperatures, for a) SMS/castor oil, and b) GMS/castor oil oleogels (G' full symbols, G'' open symbols; organogelator concentration: 20% w/w).

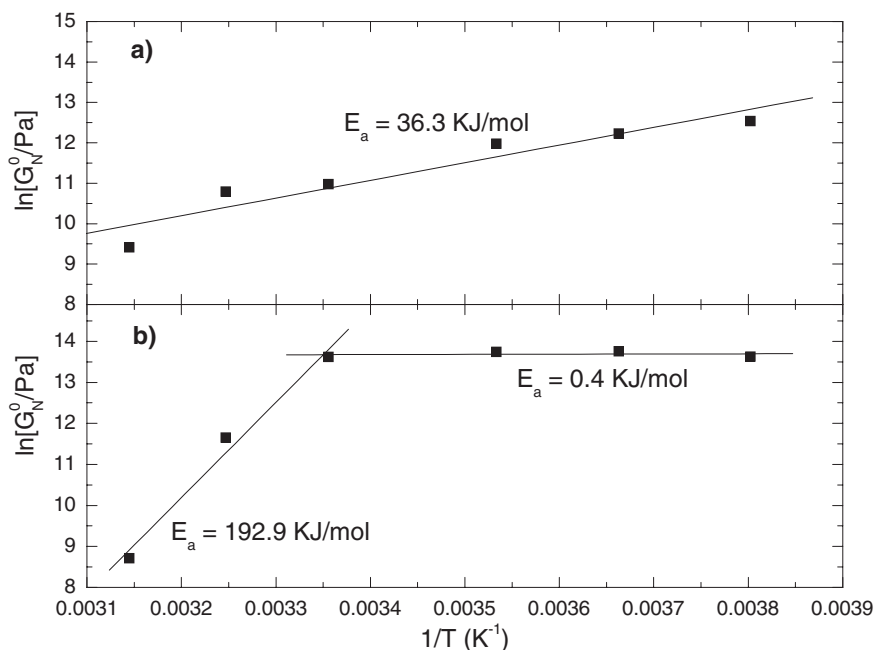


Figure 4
Evolution of the plateau modulus with temperature, and equation (1) fitting, for a) SMS/castor oil, and b) GMS/castor oil oleogels (organogelator concentration: 20% w/w).

any case, the sol-gel transition temperature of these oleogels limits their potential use as biodegradable grease formulations for low temperature in-service applications.

d) Influence of the nature of vegetable oi

As discussed elsewhere (Quinchia *et al.*, 2010), castor oil is much more viscous than the rest of conventional vegetable oils, which represents an important advantage for lubricating purposes. However, its high content in ricinoleic acid (see Table 1) yields a poor stability to oxidation. Figure 5 shows the evolution of SAOS viscoelastic functions with frequency for oleogels prepared with SMS or GMS and different vegetable oils. Some unexpected experimental results can be observed. The lowest G' and G'' values were obtained for oleogels prepared with the most viscous oil, i.e. castor oil, both for SMS- and GMS-based oleogels. On the contrary, significantly higher values of the linear viscoelastic functions were found for gels prepared with low-viscosity oils, like rapeseed and soybean oils. However, an extensive plateau region, with almost identical relative elastic characteristics in a wide frequency range (Figures 5b and 5d), was noticed in all cases. Only at the highest frequencies, lower values of the loss tangent can be observed for oleogels prepared with low-viscosity oils, especially in the case of those containing soybean oil, as a consequence of the displacement of the minimum in G'' to higher frequencies. Similar results were previously found with standard lithium soap-based lubricating greases manufactured with paraffinic oils of different viscosities (Delgado *et al.*, 2006a). Larger gel strength, associated to enhanced

elastic properties, was found in greases prepared with low-viscosity paraffinic oils. This fact was attributed to a higher solvency between the base oil and the thickening agent, which reinforces the gel network.

3.2. Lubrication performance-related properties

Some lubrication performance-related properties of the oleogels studied have been analyzed according to standard mechanical stability tests and tribological experiments, and compared with those shown by two target lithium lubricating greases, based on paraffinic and naphthenic oils, respectively (Table 2). Consistency is a widely-accepted technological parameter for lubricating greases, obviously related to the rheological behavior, which is usually evaluated in the lubricant industry through standard penetration tests. Penetration values of unworked samples are traditionally converted to NLGI grades, in order to classify greases according to their consistency degree (between 000 and 6). The most commonly used greases are those with NLGI grade 2. Softer grades, especially 0 and 1, are sometimes used for improved pumpability or low-temperature applications, while higher consistency indexes are used for certain high-speed bearings (NLGI, 1994). Table 2 collects unworked penetration values for the different oleogels studied. As can be seen, SMS-based oleogels show lower consistency values than GMS-based oleogels, being the NLGI grades of the later comparable to those displayed by mineral oil-based greases. Table 2 also includes information about the mechanical stability of the samples analyzed, determined as the difference

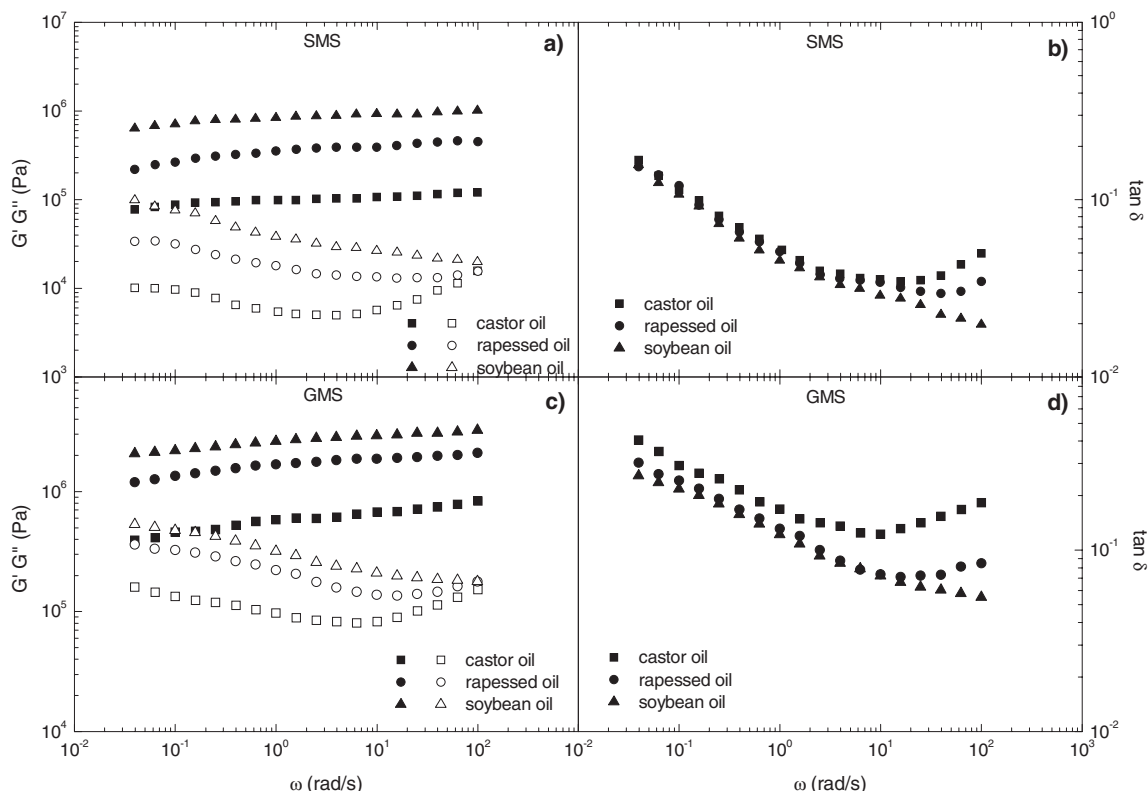


Figure 5 Frequency dependence of (a, c) the storage and loss moduli, and (b, d) the loss tangent, at 25°C, for SMS- and GMS-based oleogels containing different vegetable oils (G' full symbols, G'' open symbols; organogelator concentration: 20% w/w).

between penetration indexes after and before submitting the grease to a standard working test, in this case a shear rolling test. Greases having appropriate mechanical stability must exhibit penetration increments after working close to zero. As can be observed in Table 2, oleogel penetration values obtained after working are generally much higher than those shown by model lithium greases,

especially for SMS-based samples (> 900 dmm), which indicate a very poor mechanical stability. GMS-based oleogels exhibit much lower penetration values after working, but only the GMS/castor oil gel shows a suitable mechanical stability (penetration increment of 37 dmm). However, the oleogels studied present a high level of consistency recovery, during sample storage, after working test completion.

Table 2 Penetration values and mechanical stability for oleogel formulations and some reference lithium lubricating greases

Lubricating Grease			Unworked penetration (dmm)	NLGI grade	Worked penetration (dmm)	Penetration variation (dmm)	Recovery penetration, after 5 h at rest (dmm)	
Oil	Thickener	Thickener concentration (% w/w)						
Castor	SMS	20	415	00	> 1000	> 551	380	
	GMS		265	2	302	37	264	
Rapessed	SMS		313	1	929	616	823	
	GMS		259	2	391	132	290	
Soybean	SMS		325	1	903	578	489	
	GMS		249	3	339	90	275	
Naphthenic (*)	Lithium soap		14	274	2	289	15	–
Paraffinic (**)	Lithium soap		20	303	1-2	305	2	–

(*) data from Martin-Alfonso *et al.* (2009)
 (**) data from Delgado *et al.* (2006a)

Thus, as can be observed in Table 2, oleogel penetration values, after 5 hours ageing at rest, are similar to the unworked penetration values, especially in the case of GMS-based gels.

Finally, the potential applicability of these oleogels as biodegradable lubricating greases has been also investigated in a tribological contact. Table 3 shows the friction coefficient values, obtained in a ball-disc tribometer, for selected castor oil-based oleogel samples compared to those found for model lithium greases. As can be observed, the oleogel samples studied in this work show lower friction coefficient values than model mineral oil-based lithium greases. As previously discussed (Sanchez *et al.*, 2008), this suitable tribological response is mainly determined by the base oil employed. In this sense, Adhvaryu and co-workers (2004) pointed out that vegetable oils present optimum lubricity, lowering, more effectively, the frictional forces in comparison to other mineral oils of similar kinematic viscosities.

4. CONCLUSIONS

The rheological properties of oleogels based on sorbitan and glyceryl monostearates and different types of vegetable oils, potentially applicable as a biodegradable alternative to traditional lubricating greases, have been investigated. The linear viscoelastic response and mechanical stability of these oleogels are significantly influenced by the type and concentration of the organogelator and the vegetable oil used in the formulations. Moreover, the cooling profile applied during gelification significantly influences the rheological response of SMS-based oleogels but, on the contrary, does not affect the rheology of GMS-based oleogels. Glyceryl monostearate (GMS) generally produces stronger gels than sorbitan monostearate (SMS). The values of the linear viscoelasticity functions increase with gelling agent concentration for both types of gels, more dramatically in the case of SMS-based gels. Oleogels formulated with low-viscosity oils, such as rapeseed and soybean oils, show significantly higher values of the linear viscoelastic functions than those prepared with high-viscosity oils such as castor oil. However, an extensive plateau region in

the mechanical spectrum, with similar relative elastic characteristics, was noticed in all cases. An Arrhenius-type equation can be used to evaluate the thermo-rheological behavior of oleogels. In the case of SMS-based oleogels, a single exponential equation fits the plateau modulus-temperature dependence, in the whole temperature range studied. On the contrary, two different Arrhenius-type equations are needed to fit the evolution of GMS-based oleogels, being the values of SAOS viscoelastic functions almost constant below a critical temperature of around 35°C. Finally, the lubrication performance-related properties of oleogels have been studied by means of standard mechanical stability tests and tribological experiments. GMS-based oleogels exhibit much better mechanical stability than SMS-based oleogels, although only the GMS/castor oil gel shows a suitable mechanical stability, comparable to those found in standard lubricating greases. However, the oleogels studied present a high level of consistency recovery during storage after working test completion, as well as low values of the friction coefficient obtained in a tribological contact.

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REFERENCES

- Adhvaryu A, Erhan SZ. 2002. Epoxidized soybean oil as a potential source of high-temperature lubricants. *Ind. Crops Prod.* **15**, 247-254.
- Adhvaryu A, Erhan SZ, Perez JM. 2004. Tribological studies of thermally and chemically modified vegetable oils for use as environmentally friendly lubricants. *Wear* **257**, 359-367.
- Almeida IF, Bahia MF. 2005. Comparison of the mechanical properties of two oleogels. *e-rheo.pt* **5**, 12-18.
- Almeida IF, Bahia MF. 2006. Evaluation of the physical stability of two oleogels. *Int. J. Pharm.* **327**, 73-77.
- Delgado MA, Sánchez MC, Valencia C, Franco JM, Gallegos C. 2005. Relationship among microstructure, rheology and processing of a lithium lubricating grease. *Chem. Eng. Res. Des.* **83**, 1085-1092.
- Delgado MA, Valencia C, Sánchez MC, Franco JM, Gallegos C. 2006a. Influence of soap concentration and oil viscosity on the rheology and microstructure of lubricating greases. *Ind. Eng. Chem. Res.* **45**, 1902-1910.
- Delgado MA, Valencia C, Sánchez MC, Franco JM, Gallegos C. 2006b. Thermorheological behaviour of a lithium lubricating grease. *Tribol. Lett.* **23**, 47-54.

Table 3

Friction coefficient values for selected oleogels and reference lithium lubricating greases

Sample	Friction coefficient
Castor oil/SMS (20% w/w)	0.063
Castor oil/GMS (20% w/w)	0.057
Naphthenic oil/lithium soap (14% w/w)	0.090
Paraffinic/lithium soap (20% w/w)	0.105

- Erhan SZ, Asadauskas S. 2000. Lubricant basestocks from vegetable oils. *Ind. Crops Prod.* **11**, 277-282.
- Erhan SZ, Sharma BK, Perez JM. 2006. Oxidation and low temperature stability of vegetable oil-based lubricants. *Ind. Crops Prod.* **24**, 292-299.
- Ferry JD. 1980. *Viscoelastic properties of polymers*. John Wiley and Sons, New York.
- Franco JM, Guerrero A, Gallegos C. Influencia de las concentraciones de aceite y emulsionante en las propiedades reológicas de emulsiones aceite en agua del tipo salsa fina. 1995. *Grasas y Aceites* **46**, 108-114.
- Franco JM, Delgado MA, Valencia C, Sánchez MC, Gallegos C. 2005. Mixing rheometry for studying the manufacture of lubricating greases. *Chem. Eng. Sci.* **60**, 2409-2418.
- Gallegos C, Franco JM, Partal P. 2004. Rheology of food dispersions, in Binding DM, Walters K (Ed.) *Rheology Reviews 2004*, The British Society of Rheology, Aberystwyth, pp 19-65.
- García-Zapateiro LA, Delgado MA, Franco JM, Valencia C, Ruiz-Méndez MV, Garcés R, Gallegos C. 2010. Oleins as a source of estolides for biolubricant applications, *Grasas y Aceites*, **61**, 171-174.
- Heng PWS, Chan LW, Chow KT. 2005. Development of novel nonaqueous ethylcellulose gel matrices: rheological and mechanical characterization. *Pharm. Res.* **22**, 676-684.
- Hinze WL, Uemasu I, Dai F, Braun JM. 1996. Analytical and related applications of organogels. *Curr. Opinion Colloid & Interface Sci.* **1**, 502-513.
- Lizaso E, Muños ME, Santamaría A. 1999. Formation of gels ethylcellulose solutions. An interpretation from dynamic viscoelastic results. *Macromolecules* **32**, 1883-1889.
- Martín-Alfonso JE, Valencia C, Sánchez MC, Franco JM, Gallegos C. 2007. Development of new lubricating grease formulations using recycled LDPE as rheology modifier additive. *Eur. Polym. J.* **43**, 139-149.
- Martín-Alfonso JE, Valencia C, Sánchez MC, Franco JM, Gallegos C. 2009. Rheological modification of lubricating greases with recycled polymers from different plastics waste. *Ind. Eng. Chem. Res.* **48**, 4136-4144.
- Mewis J, Spaul AJB. 1976. Rheology of concentrated dispersions. *Adv. Colloid Interface Sci.* **6**, 173-200.
- NLGI. 1994. *Lubricating Grease Guide*. National Lubricating Grease Institute, Kansas.
- Nunes MC, Raymundo A, Sousa I. 2006. Rheological behaviour and microstructure of pea protein/k-carrageenan/starch gels with different setting conditions. *Food Hydrocolloids* **20**, 106-113.
- Quinchia LA, Delgado MA, Valencia C, Franco JM, Gallegos C. 2009. Viscosity modification of high-oleic sunflower oil with polymeric additives for the design of new biolubricant formulations. *Environ. Sci. Technol.*, **43**, 2060-2065.
- Quinchia LA, Delgado MA, Valencia C, Franco JM, Gallegos C. 2010. Viscosity modification of different vegetable oils with EVA copolymer for lubricant applications. *Ind Crops Prod.* **32**, 607-612.
- Ruiz-Márquez D, Partal P, Franco JM, Gallegos C. 2010. Emulsiones alimentarias aceite-en-agua estabilizadas con proteínas de atún. *Grasas y Aceites* **61**, 352-360.
- Sánchez R, Franco JM, Delgado MA, Valencia C, Gallegos C. 2008. Effect of thermo-mechanical processing on the rheology of oleogels potentially applicable as biodegradable lubricating greases. *Chem. Eng. Res. Des.* **86**, 1073-1082.
- Sánchez R, Franco JM, Delgado MA, Valencia C, Gallegos C. 2011. Thermal and mechanical characterization of cellulosic derivatives-based oleogels potentially applicable as bio-lubricating greases: influence of ethyl cellulose molecular weight. *Carbohydr. Polym.* **83**, 151-158.
- Wilson B. 1998. Lubricants and functional fluids from renewable sources. *Ind. Lubr. Tribol.* **50**, 6-15.
- Zhong Q, Dauber CR, Velev OD. 2004. Cooling effects on a model rennet casein gel system: part II. Permeability and microscopy. *Langmuir* **20**, 7406-7411.

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