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# Effect of thermo-mechanical processing on the rheology of oleogels potentially applicable as biodegradable lubricating greases

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## ABSTRACT

This work is focused on the development of oleogels potentially suitable as biodegradable lubricating greases by studying the effect that some thermo-mechanical processing variables exert on their rheological properties and microstructure. Oleogels were prepared by dispersing sorbitan monostearate (SMS) in castor oil under different agitation conditions and thermal protocols. The effect of processing variables was evaluated by performing small-amplitude oscillatory shear (SAOS) measurements, AFM observations and some mechanical and tribological tests usually employed to check lubrication performance and stability of lubricating greases. Rheological properties of oleogels can be monitored *in situ* during processing using a rheo-reactor. Processing conditions such as maximum temperature applied to disperse the gelling agent, heating time, agitation speed and cooling rate significantly influence gel strength. Cooling profile is the most important processing variable affecting the rheological response of oleogels. Differences of more than one decade in the values of SAOS functions were found for oleogels processed by applying different cooling profiles. A moderate agitation during SMS dispersion in oil yields maximum values of oleogel linear viscoelasticity functions. The maximum processing temperature reached during this stage should be only slightly higher than the SMS melting point. In general, oleogel samples exhibited a poor mechanical stability after sample working in a rolling element, but, on the contrary, they recovered completely their initial consistency after a moderate resting time, also exhibiting remarkable lubricant properties. Moreover, oleogel samples tested in a ball-disc tribometer show values of the friction coefficient inferior to those obtained with model lithium lubricating greases.

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## 1. Introduction

Oleogels are complex microstructured systems composed of an organic hydrophobic solvent and a substance, frequently an amphiphilic molecule, able to form a three-dimensional network which immobilizes the continuous medium. Nowadays, the main applications of oleogels are found in the field of pharmaceuticals and cosmetics (Hinze *et al.*, 1996). In particular, sorbitan esters have been successfully tested as organogelators (Murdan *et al.*, 2005; Almeida and Bahia, 2006). However, these studies have been mainly focused on the physical stability and microstructure of oleogels. Thus, little attention has

been paid to the optimization of the processing protocol necessary to form these oleogels.

On the other hand, up to now, other potential applications of oleogels have not been explored. Nowadays, one of the main problems of very different industrial sectors concerns the impact that process technologies and products cause in the environment. In this sense, there is a general tendency to promote both the replacement of non-renewable raw materials by renewable resources, and the minimization of the environmental impact caused by industrial waste materials. Concerning the impact that lubricants exert on the environment, every year millions of tonnes of engine, industrial and

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hydraulic oils are leaked into the ground or motorways, or are poured in the environment. Even small amounts of these products can inhibit the growth of trees and can be toxic to aquatic life (Wilson, 1998). In this sense, a slow but steady movement toward the use of “environmentally friendly” or more readily biodegradable lubricants has been noticed during the last decade. Erhan and co-workers (Erhan and Asadauskas, 2000; Erhan et al., 2006; Adhvaryu and Erhan, 2002; Adhvaryu et al., 2004) and Dicken (1994) have reported the advantages and disadvantages of using 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 also present good lubricity and ability for adhering to metal surfaces, low volatility, small viscosity–temperature dependence and, of course, non-toxicity and high biodegradability.

The development of environmentally friendly lubricating grease formulations based on 100% biodegradable raw materials seems to present much more difficulty. Greases may be considered gel-like colloidal suspensions in which a suitable thickener is dispersed in a lubricating liquid, traditionally a mineral or synthetic oil (NLGI, 1994). As Adhvaryu et al. (2005) reported, a more biodegradable formulation can be obtained just replacing the mineral oil by a vegetable one. However, the substitution of the thickener agents traditionally used (metallic soaps, phyllosilicates or polyurea compounds) by others more environmentally acceptable has not yet been considered. The traditional thickeners, especially metallic soaps, confer to greases their main functional properties, among others gel-like characteristics and suitable rheological properties, but cannot be considered as biodegradable materials. Obviously, finding a biodegradable thickener agent with suitable properties may create a new market niche with interesting perspectives for the future (Fessenbecker, 2003). In this sense, although some limitations, especially related to maximum working temperature (which otherwise depends on the solvent (Murdan et al., 2005)), are apparent, oleogel formulations based in vegetable oils may offer some benefits as a biodegradable alternative to greases, at least for specific applications.

As previously reported (Delgado et al., 2005; Franco et al., 2005), the manufacturing process of traditional lubricating greases is highly complex, with many thermo-mechanical variables affecting the final properties of this product, i.e. rheological behaviour and mechanical stability among others. Basically, the manufacture of lubricating greases, with generation *in situ* of the soap thickener during the mixing process, consists of the saponification reaction of fatty acids, followed by dehydration, heating up to near the phase transition temperature of soap crystallites and cooling down to crystallize the soap (Hamnelid, 2000). Similarly, it is well-known that the gel formation mechanism is also affected by the processing variables, especially by the thermal protocol selected (Moros et al., 2003; Nunes et al., 2006; Zhong et al., 2004). The aim of this work was focused on the development of some oleogels, potentially useful as biodegradable lubricating greases, by studying the effect that some thermo-mechanical processing variables exert on the rheological properties and microstructure of oleogels. In addition to this, some mechanical and tribological tests, usually employed to confirm the lubrication performance and stability of greases, have been carried out with oleogel formulations, in order to test their suitability as lubricants.

**Table 1 – Kinematic viscosity values, at 40 °C, for the different oils used**

Oil	Kinematic viscosity (cSt)
Naphtenic	110
Paraffinic 1	334
Paraffinic 2	105
Castor	211

## 2. Materials and methods

### 2.1. Materials

Castor oil (Guinama, Spain) was used as the biodegradable raw material to prepare oleogel formulations. Sorbitan monostearate (SMS) of HLB=4.7 (Panreac, Spain) was used as the gelling agent. Standard lithium 12-hydroxystearate lubricating greases were used as reference systems. 12-hydroxystearic acid, hydrated lithium hydroxide, and paraffinic and naphthenic mineral oils were kindly supplied by Verkol Lubricantes S. A. (Spain). Values of kinematic viscosities, at 40 °C, of the different oils used in these grease formulations are listed in Table 1.

### 2.2. Manufacture of oleogel formulations

Processing of oleogels was performed in an open vessel, using an anchor impeller geometry ( $D=90$  mm;  $H=110$  mm) to disperse the gelling agent. Batches of 600 g were prepared, employing in all cases a SMS concentration of 20% (w/w). SMS was dispersed in the vegetable oil under agitation (60–150 rpm) at different temperatures, comprised between SMS melting point ( $\approx 58$  °C) and 80 °C, and for different mixing times, ranging from 15 to 60 min. It is worth pointing out that the application of temperatures lower than the SMS melting point does not yield a homogeneous gel. Then, the solution was cooled down to room temperature in order to induce gelification. Cooling was carried out either by switching off the thermostatic device, or placing the vessel into a large quenching system of water at 0, 5 or 25 °C, under mild agitation. In addition, several oleogel agitation speeds (0–150 rpm) during cooling were tested.

### 2.3. Rheological characterization

Rheological characterization of oleogels was carried out with both a Rheoscope controlled-stress rheometer (TermoHaake, Germany), and an ARES controlled-strain rheometer (Rheometrics Scientific, UK). Small-amplitude oscillatory shear (SAOS) tests were performed inside the linear viscoelastic region, using a rough plate–plate geometry (20 mm, 1 mm gap, relative roughness 0.4), in a frequency range of  $10^{-2}$  to  $10^2$  rad/s. At least two replicates of each test were performed on fresh samples. Fig. 1 illustrates the sample-to-sample variability in SAOS functions for a selected system. Rheological tests were always carried out at 25 °C.

Occasionally, *in situ* viscosity measurements during processing were monitored using the ARES rheometer equipped with a cylindrical rheo-reactor (40 mm diameter, 48 mm height) and an anchor mixing geometry (38 mm diameter) coupled with the transducer of the rheometer. This tool allows one to monitor the evolution of viscosity with time during processing, as well as to accomplish further rheological measurements after the mixing process (Nachbaur et al., 2001).

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