

## **Gel-like Dispersions Based on Cellulosic Derivatives and Castor Oil Applicable as Biodegradable Lubricating Greases**

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This study deals with the design of gel-like dispersions formulated using castor oil and ethyl cellulose/ $\alpha$ -cellulose or ethyl cellulose/methyl cellulose blends, potentially applicable as bio-lubricating greases. The influences of ethyl cellulose molecular weight and cellulosic derivatives concentration ratio ( $W$ ) on the thermal behaviour, linear viscoelasticity and mechanical stability were studied. Experimental results show that small-amplitude oscillatory shear (SAOS) functions are not significantly influenced by ethyl cellulose molecular weight below a critical threshold value ( $M_w < 70000$  g/mol). On the contrary, a significant increase in SAOS functions is noticed using ethyl cellulose with  $M_w$  values higher than the critical one. Temperature does not have a significant influence on SAOS functions, which is opposite to the behaviour found with standard lubricating greases. On the other hand, all oleogel formulations studied display much higher decomposition temperatures than standard lubricating greases, independently of both ethyl cellulose molecular weight and concentration ratio. Formulations containing ethyl cellulose/methyl cellulose blends show excellent mechanical stability enhanced by increasing ethyl cellulose molecular weight. A decrease in the values of the linear viscoelasticity functions down to a minimum value was found by increasing ethyl cellulose/ $\alpha$ -cellulose or ethyl cellulose/methyl cellulose weight ratios ( $W$ ) up to a critical value. Above this, the linear viscoelastic functions increase with  $W$ , at temperatures in the range 0-75°C, and continuously decrease at higher temperatures, i.e. 125°C.

### **1. Introduction**

Lubricating greases are highly structured suspensions, traditionally consisting of a thickener dispersed in mineral or synthetic oil (Delgado et al., 2006a). Fatty acid soaps of lithium, calcium, sodium, aluminium or barium are most commonly used as thickeners (NLGI, 1994) inducing to the lubricating grease gel-like characteristics and appropriate rheological properties (Madedo et al., 2000). Nowadays, lubricating manufactures are interested in completely biodegradable products or at least more environmentally acceptable. The use of standard lubricating greases increases pollution and damages natural resources (Wilson, 1998). The first step made to produce a

friendlier lubricating product consisted in the replacement of the mineral oil by a vegetable one (Stempfel, 1998). However, the consecution of completely biodegradable lubricating greases also implies the replacement of traditional metallic soaps by natural thickeners. The main objective of this research is to test different cellulose derivatives as thickener agents, not previously used for this application, in order to obtain different gel-like suspensions in a castor oil medium which has been widely used as biolubricant. The influence of ethyl cellulose molecular weight and concentration ratio of thickeners on the properties of oleogels was particularly explored.

## 2. Materials and Methods

### 2.1 Materials

Castor oil (211 cSt at 40 °C, Guinama, Spain) was selected as biodegradable lubricating oil. Five ethyl cellulose samples (48% ethoxy content) differing in molecular weight ( $M_w$ : 39000, 53000, 69000, 77000, 82000 g/mol), methyl cellulose ( $M_n$  40000 g/mol; 32% methoxy content), and partially microcrystalline  $\alpha$ -cellulose, all of them from Sigma-Aldrich, were used as thickener agents to prepare different gel-like dispersions.

### 2.2 Preparation of oleogel formulations

Oleogels were processed using a helical ribbon impeller geometry. Firstly the corresponding amounts of oil and ethyl cellulose (2%) were mixed at 150°C. The other cellulosic derivatives employed in the formulation (20%  $\alpha$ -cellulose or 30% methyl cellulose) were added once the ethyl cellulose was completely dissolved, and blended for 30 minutes. Finally, the mixture was cooled down to room temperature by natural convection. Weight ratio between ethyl cellulose and the other cellulose derivative was also changed from 0.06 to 0.14 for  $\alpha$ -cellulose and from 0.04 to 0.12 for methyl cellulose, by keeping the total amount of cellulosic derivatives in 22% and 27% respectively.

### 2.3 Thermogravimetric analysis (TGA)

Thermogravimetric analysis was carried out with a Q-50 TA Instrument. Approximately, 15 mg of each sample were placed on a Pt pan, and heated from 30 °C to 600 °C, at 10 °C/min, under  $N_2$  total flow of 100 mL/min.

### 2.4 Rheological characterization

Rheological characterization was carried out in a controlled-stress rheometer (RS-150, ThermoHaake, Germany). Small-amplitude oscillatory shear (SAOS) tests were performed inside the linear viscoelastic region, using a plate-plate geometry (35 mm, 1 mm gap), in a frequency range of  $10^{-2}$ – $10^2$  rad/s, and temperatures comprised between 0 and 225 °C. At least two replicates of each test were performed on fresh samples.

### 2.5 Penetration and mechanical stability tests

Both unworked and worked penetration indexes were determined according to the ASTM D 1403 standard, by using a Seta Universal penetrometer, model 17000-2 (Stanhope-Seta, UK), with one-quarter cone geometry. The one-quarter scale penetration values were converted into the equivalent full-scale cone penetration values, following the ASTM D 217 standard. Samples were worked during 2 hours in a Roll

Stability Tester, model 19400-3 (Stanhope-Seta, UK) according to the ASTM D 1831 standard, and penetration measurements were performed after this test.

### 3. Results and Discussion

Figure 1 shows the frequency dependence of the linear viscoelasticity functions for gel-like  $\alpha$ -cellulose (a) or methyl cellulose (b) suspensions in castor oil media containing several ethyl celluloses with different molecular weights. This dependence is qualitatively similar to that found for standard lubricating greases (Madiedo, 2000).  $G'$  and  $G''$  are not significantly influenced by ethyl cellulose molecular weight for  $M_w < 70000$  g/mol. For those oleogels containing  $\alpha$ -cellulose, a significant increase in both SAOS functions is noticed when using ethyl cellulose with  $M_w$  higher than this critical one and the minimum in  $G''$  is shifted to higher frequencies. In the case of oleogels formulated with methyl cellulose, only a significant increase in  $G'$  is observed for the oleogel containing ethyl cellulose with the highest molecular weight.

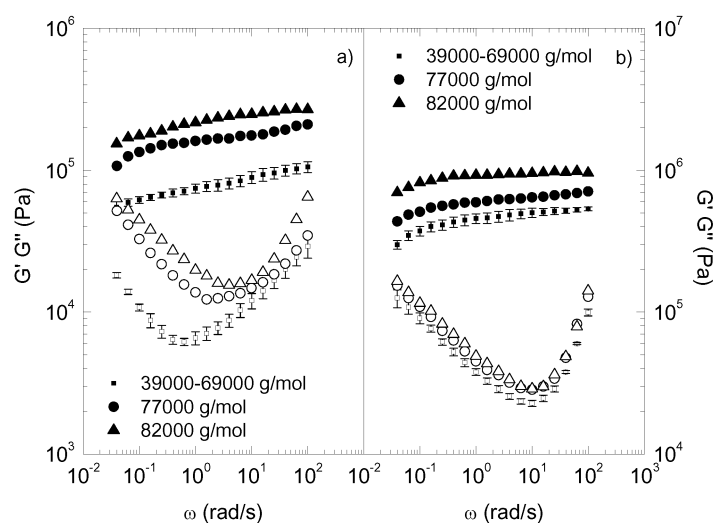


Figure 1: Evolution of the storage (filled symbols) and loss (open symbols) moduli with frequency for oleogels formulated with  $\alpha$ -cellulose (a) or methyl cellulose (b) and different number average molecular weight ( $M_w$ ) ethyl cellulose at 25 °C (standard deviation bars were included for  $M_w < 70000$  g/mol).

As previously reported for standard lithium greases (Delgado et al., 2006b), the plateau modulus can be used to quantify the influence of temperature by using an Arrhenius-type equation. The activation energy ( $E_a$ ) evaluates the thermal dependence. The mean activation energy values for oleogels thickened with  $\alpha$ -cellulose and methyl cellulose are 5.4 kJ/mol and 4.1 kJ/mol, respectively. These values are higher than those obtained for standard lithium greases in the low-temperature range (1-2 kJ/mol), but much lower than those found in the high-temperature range (18-20 kJ/mol).

Figure 2 shows oleogels based on ethyl cellulose/ $\alpha$ -cellulose (a) or ethyl cellulose/methyl cellulose (b) blends with different weight ratios. As can be observed, dispersions with the lowest weight ratios show significantly higher values of both  $G'$  and  $G''$ . A dramatic decrease in both SAOS functions is noticed by increasing the weight ratio until a critical value where a further increase in  $W$  produces the opposite effect. This behaviour is noticed at temperatures ranging from 0 °C to 75 °C but not found at 125 °C, where SAOS functions continuously decrease with  $W$ . It can be attributed to the sol-gel transition of ethyl cellulose in castor oil, which takes place around 70°C.

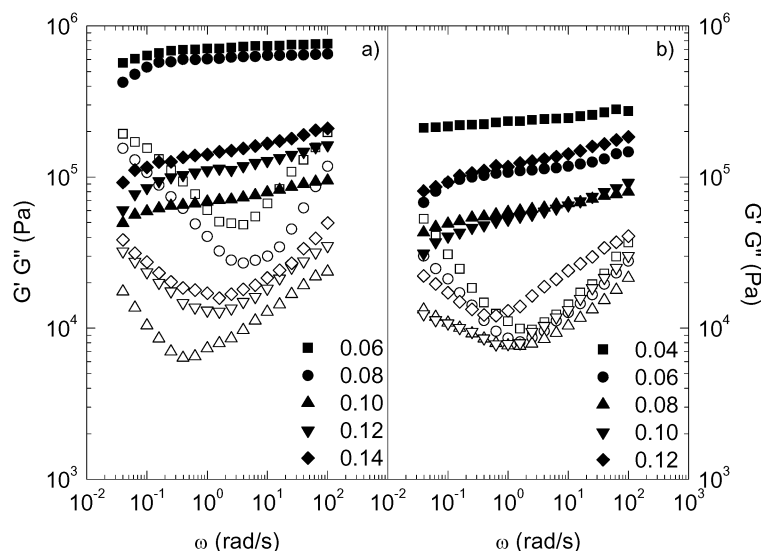


Figure 2: Evolution of the storage (filled symbols) and loss (open symbols) moduli with frequency for oleogels formulated with  $\alpha$ -cellulose (a) or methyl cellulose (b) using different weight ratio ( $W$ ) at 25 °C.

Thermal susceptibility in the plateau modulus increases at high weight ratios for both types of oleogels. Activation energy values are clearly increased selecting high values of weigh ratio reaching values around 15 and 40 kJ/mol for oleogels thickened with  $\alpha$ -cellulose or methyl cellulose respectively.

Table 1 displays mechanical stability values for these oleogels and some thermogravimetric parameters described in Sánchez et al. (2009). Specifically, oleogels based on  $\alpha$ -cellulose always show similar unworked penetration values, independently of ethyl cellulose molecular weight. However, oleogels containing ethyl cellulose with the highest molecular weights shows the highest worked penetration values, yielding the worst mechanical stability. On the other hand, both unworked and worked penetration values clearly decrease by increasing ethyl cellulose molecular weight for methyl cellulose-based oleogels. Moreover, the penetration values are generally lower than those found in oleogels with  $\alpha$ -cellulose. Most important is the improved mechanical stability showed by oleogels containing ethyl cellulose with high molecular weight. On

the other hand, oleogels with different W values show very low consistency especially when dispersions were formulated with ethyl cellulose/methyl cellulose blends. However, these cellulose derivatives yield oleogels formulations with appropriate mechanical stability values, similar to those found for standard greases. In addition to mechanical stability, thermal resistance is another important issue for biolubricant formulations. As can be observed, these oleogels can resist high temperatures without losing a significant amount of mass with  $T_{\text{onset}}$  values higher than those obtained for standard lubricating greases (around 190 °C). Oleogel thermal stability is significantly influenced neither by ethyl cellulose molecular weight nor by weight ratio, but it is clearly affected by the nature of the second cellulose derivative employed as thickener. It is apparent that the formulations containing  $\alpha$ -cellulose show the best thermal stability (Sánchez et al., 2009)

Table 1: Penetration and characteristic decomposition temperatures for oleogels

Main thickener	Ethyl cellulose $M_w$ (g/mol)	W	Unworked penetration (dmm)	Worked penetration (dmm)	Penetration variation (dmm)	$T_{\text{onset}}$ (°C)
$\alpha$ -cellulose	39000	0.10	384	474	90	352.0
	53000	0.10	377	470	94	
	69000	0.10	380	467	86	
	77000	0.10	377	485	109	
	82000	0.10	369	504	135	
	69000	0.06	335	407	71	
	69000	0.08	343	418	75	
	69000	0.12	358	433	75	
	69000	0.14	354	433	79	
	methyl cellulose	39000	0.07	380	392	
53000		0.07	369	377	8	
69000		0.07	324	332	8	
77000		0.07	294	298	4	
82000		0.07	275	279	4	
69000		0.04	429	422	-7	
69000		0.06	440	440	0	
69000		0.08	422	425	3	
69000		0.10	410	410	0	
69000		0.12	425	429	4	

#### 4. Conclusions

Addition of ethyl cellulose with different molecular weights or changes in ethyl cellulose/ $\alpha$ -cellulose or ethyl cellulose/methyl cellulose weight ratios yields oleogel formulations with different rheological, thermal and mechanical properties some of them with suitable characteristics to be employed as lubricating greases. From a rheological point of view, oleogels SAOS functions are influenced by ethyl cellulose

molecular weight only above a critical value ( $M_w < 70000$  g/mol). Moreover, temperature does not influence their qualitative dependence on frequency. An important decrease in the values of the linear viscoelasticity functions down to a minimum value has been found by increasing ethyl cellulose/ $\alpha$ -cellulose or ethyl cellulose/methyl cellulose weight ratio ( $W$ ) up to a critical value, which depends on both the nature of the cellulosic derivatives employed and temperature. Above this critical value, the viscoelastic functions increase with  $W$ , at temperatures ranging from 0 to 75°C. However, at higher temperatures, i.e. 125°C, a continuous decrease in the values of SAOS viscoelastic moduli with  $W$  has been always observed. The thermal dependence of the “plateau” modulus increases significantly with ethyl cellulose concentration in oleogels thickened with both ethyl cellulose/ $\alpha$ -cellulose and ethyl cellulose/methyl cellulose blends.

Oleogel formulations studied display much higher decomposition temperatures than standard lubricating greases, independently of ethyl cellulose molecular weight and weight ratios. Finally, it is worth remarking that oleogels formulated with ethyl cellulose/methyl cellulose blends show appropriate mechanical stability, which is enhanced by increasing ethyl cellulose molecular weight.

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