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Thermal and mechanical characterization of cellulosic derivatives-based oleogels potentially applicable as bio-lubricating greases: Influence of ethyl cellulose molecular weight

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ABSTRACT

This work deals with the design of new gel-like formulations based on blends of cellulosic derivatives and castor oil, which could be potentially applicable as environmentally-friendly lubricating greases. In particular, the influence of ethyl cellulose molecular weight, blended with α-cellulose or methylcellulose, on the thermal and rheological properties of the resulting gel-like dispersions was explored. Thermal and rheological behaviours were characterized by means of TGA tests and linear viscoelasticity (SAOS) measurements. Moreover, some standard mechanical tests, usually performed on commercial lubricating greases, were carried out in order to evaluate the suitability of these oleogels for lubricant applications. From the experimental results obtained, it can be deduced that SAOS functions of gel-like dispersions are not significantly influenced by ethyl cellulose molecular weight below a critical threshold value ($M_w < 70{,}000$ g/mol). On the contrary, a significant increase in both SAOS functions is noticed when using ethyl cellulose with M_w values higher than the critical one. Moreover, temperature does not have a large influence on oleogels SAOS functions, which is opposite to the behaviour found with standard lubricating greases. Formulations containing methylcellulose/ethyl cellulose blends show excellent mechanical stability parameters, enhanced by increasing ethyl cellulose molecular weight. On the other hand, all the oleogel formulations studied display much higher decomposition temperatures than standard lubricating greases, independently of ethyl cellulose molecular weight.

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1. Introduction

Nowadays, there is a continuous tendency to improve the performance of industrial processes and machineries. Concerning mechanical elements submitted to movement, friction reduction is one of the main goals. Design of more efficient lubricants is, then, necessary to reach this objective. However, the industry of lubricants is not only interested in the manufacture of new lubricants for enhanced mechanical performance, but also on improved products from an environmental point of view. In this sense, mostly in the last two decades, lubricant customers are aware of the negative effects that traditional lubricants exert on the environment and, therefore, are demanding new green products able to reduce this impact. In addition to this, the increase in the use of eco-friendly materials has been promoted as a result of strict government regulations that some countries are adding in their legislation (Adhvaryu & Erhan, 2002; Beran, 2008). In fact, the use of biodegradable lubricants is not an innovative idea (i.e., 4000 B.C. natural fats were used for cart wheels lubrication). Lately, biolubricants are of increasing importance for different applications like engines, gears and transmissions (Lea, 2002).

Standard lubricating grease formulations are gel-like colloidal suspensions in which a suitable thickener, usually a metallic soap, is dispersed in a mineral or synthetic oil (NLGI, 1994), both components considered non-biodegradable materials. Obviously, the generalized use of these formulations for different applications incorporates part of these products into the environment, thus increasing pollution and destroying natural resources (Beran, 2008; Wilson, 1998). The first step made to produce a friendlier lubricating grease formulation was the replacement of the mineral oil, the main component (70–95%, w/w), by a vegetable one (Stempfel, 1998). Using vegetable oil in the lubricant formulations reduces environmental pollution, since it is high biodegradable (Beran, 2008; Maleque, Masjuki, & Sapuan, 2003). Vegetable oils have many other advantages, such as low toxicity, low evaporation, high load carrying abilities, naturally multigrade, good solver power for additives, etc. On the contrary, these raw materials also present certain disadvantages, for instance, low-temperature performance, low oxidation stability and high costs (Fox & Stachowiak, 2007; Jayadas & Prabhakaran Nair, 2006; Lea, 2002).

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Table 1
Fatty acid composition of the castor oil used to prepare oleogels.

Fatty acid	% (w/w)
Palmitic acid (C16:0)	2.6
Estearic acid (C18:0)	2.7
Oleic acid (C18:1)	6.3
Linoleic acid (C18:2)	10.8
Ricinoleic acid (12-hydroxy C18:1)	77.6

However, complete biodegradable lubricating grease will imply not only the replacement of the mineral oil by a suitable vegetable one, but also using natural thickener agents, which can suitably play the role of traditional metallic soaps or polyureas. As has been mentioned before, oil substitution has been satisfactorily addressed (Dresel, 1994), and some products are being sold as biodegradable greases, although they still contain a non-biodegradable thickener agent in their formulations. Consequently, the main objective of this research was to test different natural thickeners, which combined with suitable vegetable oils would yield biodegradable greases with appropriate performance. In a previous study (Sánchez, Franco, Delgado, Valencia, & Gallegos, 2009), different gel-like cellulosic derivatives suspensions in a castor oil medium were proposed as potential substitutes of lubricating greases for some applications. Cellulosic derivatives present some advantages as lubricating grease thickeners. They are biodegradable biopolymers obtained from the most abundant natural polymer (Rimdusit, Jingjid, Damrongsakkul, Tiptipakorn, & Takeichi, 2008) and, on the other hand, they can provide suitable rheological properties to these formulations (Park & Ruckenstein, 2001). In particular, the use of ethyl cellulose combined with other cellulose derivatives, i.e. methylcellulose or α-cellulose, yields gel-like dispersions with acceptable thermal, rheological and mechanical properties. The term “oleogel” was used according to the definition proposed by Almdal, Dyre, Hvidt, and Kramer (1993) for solid-like gels attending to the dynamic rheological properties, which otherwise fits the rheological response of traditional lubricating greases. As it was previously reported (Sánchez et al., 2009), the role of ethyl cellulose, by increasing oil viscosity, is essential to impart long-term physical stability to these oleogels. In this work, the influence of ethyl cellulose molecular weight on the thermal and rheological properties of oleogels based on castor oil and different cellulosic derivatives was explored. Moreover, some standard mechanical stability tests, usually performed on lubricating greases, were carried out in order to evaluate the suitability of these oleogels for lubricant applications.

2. Materials and methods

2.1. Materials

Castor oil (211 cSt at 40 °C, Guinama, Spain) was selected as biodegradable lubricating oil. The fatty acid composition of the castor oil used is shown in Table 1. Five ethyl cellulose samples (48% ethoxy content) differing in molecular weight (see Table 2), methylcellulose (M_n 40,000 g/mol; 32% methoxy content), and partially microcrystalline α-cellulose (Park, Johnson, Ishizawa, Parilla, & Davis, 2009), all of them from Sigma–Aldrich, were used as thickener agents to prepare different gel-like dispersions. The degree of polymerization (DP) for α-cellulose sample, determined according to the SCAN-C15 official method, was DP = 1011, obtained inserting the intrinsic viscosity ([η] = 438 cm^3/g) in the following equation (Gericke, Schlufter, Liebert, Heinze, & Budtova, 2009):

$$\mathrm{DP}^{0.76} = \frac{[\eta]}{2.28} \quad (1)$$

Table 2
Weight average molecular weight (M_w), number average molecular weight (M_n) and polydispersity index (M_w/M_n) of the ethyl cellulose used in the manufacture of oleogels.

Ethyl cellulose	M_n (g/mol)	M_w (g/mol)	M_w/M_n
EC1	2.4×10^4	3.9×10^4	1.60
EC2	3.6×10^4	5.3×10^4	1.46
EC3	6.0×10^4	6.9×10^4	1.15
EC4	6.9×10^4	7.7×10^4	1.12
EC5	7.5×10^4	8.2×10^4	1.09

Table 3
Formulations and codes of the processed oleogels.

Code	Ethyl cellulose		α-Cellulose (%)	Methylcellulose (%)
	(%)	M_w (g/mol)		
COEC1αC	2	3.9×10^4	20	0
COEC2αC	2	5.3×10^4	20	0
COEC3αC	2	6.9×10^4	20	0
COEC4αC	2	7.7×10^4	20	0
COEC5αC	2	8.2×10^4	20	0
COEC1MC	2	3.9×10^4	0	30
COEC2MC	2	5.3×10^4	0	30
COEC3MC	2	6.9×10^4	0	30
COEC4MC	2	7.7×10^4	0	30
COEC5MC	2	8.2×10^4	0	30

Standard lithium 12-hydroxystearate lubricating greases (14 and 20% lithium soap, NLGI grade 2) were used as benchmarks. 12-Hydroxystearic acid, lithium hydroxide, and paraffinic (334 cSt at 40 °C) and naphthenic (115 cSt at 40 °C) oils, kindly supplied by Verkol Lubricantes S.A. (Spain), were used to prepare the oleogels, using the methodology reported elsewhere (Delgado, Sánchez, Valencia, Franco, & Gallegos, 2005; Delgado, Valencia, Sánchez, Franco, & Gallegos, 2006a; Franco, Delgado, Valencia, Sánchez, & Gallegos, 2005).

2.2. Preparation of oleogel formulations

Oleogel batches (400 g) were processed in an open vessel, using a helical ribbon impeller geometry (D = 90 mm; H = 90 mm) to disperse the thickener agents. In the first step, the vessel was filled with the corresponding amounts of oil and ethyl cellulose. A constant rotational speed (60 rpm) was then applied to the mixture, while heating up to 150 °C. The other cellulosic derivatives employed in the formulation were added once the ethyl cellulose was completely dissolved, and blended at the same rotational speed and temperature, for 30 min. Finally, the mixture was cooled down to room temperature by natural convection, achieving gel-like suspensions of α-cellulose or methylcellulose in the castor oil medium modified with the ethyl cellulose. Table 3 shows the compositions of the different formulations studied, as well as the codes used for further reference. Thickener concentration was previously optimized, taking into consideration both physical stability and rheological properties similar to those found with standard lubricating greases (Sánchez et al., 2009).

2.3. Gas chromatography (GC)

GC analysis was performed with an Agilent 6890 chromatograph, equipped with a flame-ionization detector, in order to determine the fatty acid profile in castor oil. C14–C24 FAMEs provided standards were used.

2.4. Gel permeation chromatography (GPC)

Molecular weight data of ethyl cellulose samples were determined by means of the GPC technique, using a Waters apparatus, equipped with a styragel HR 4E column (7.8 mm × 300 mm), at 35 °C, and using THF as eluent. A Waters 2414 refractive index detector was used. The flow rate was 1.0 mL/min. The number average molecular weight (M_n), the weight average molecular weight (M_w), and polydispersity index (M_w/M_n) were calculated relative to poly(styrene) standards.

2.5. 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 or O_2 total flow of 100 mL/min.

2.6. Rheological characterization

Rheological characterization of oleogels was carried out in two controlled-stress rheometers (RS-150 and Rheoscope, 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 °C and 225 °C. The viscous flow behaviour of ethyl cellulose/castor oil binary systems was measured in a shear rate range of 10^{-2}–10^{2} s^{-1}. At least two replicates of each test were performed on fresh samples.

2.7. 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. Classical consistency NLGI grade was established according to these penetration values (NLGI, 1994). Samples were worked during 2 h in a Roll Stability Tester, model 19400-3 (Stanhope-Seta, UK) according to the ASTM D 1831 standard, and penetration measurements were performed, once again, immediately after this rolling test.

2.8. Leakage tendencies in wheel bearings

Oleogel leakage tendencies were determined in a wheel bearing equipment, model 17-0450 (Petrotest, Germany), according to the ASTM D 1263 standard. This test method evaluates the leakage tendency of lubricating greases when they are tested under specific simulated wheel bearing conditions. The sample was distributed in a modified front-wheel hub and spindle assembly. The hub rotated, at a speed of 660 ± 30 rpm for 6 h ± 5 min, at a spindle temperature, which was raised to and then maintained, of 105 ± 1.2 °C. The same test was also performed at room temperature. Leakage of the sample was measured, and the condition of the bearing surface was checked at the end of the test.

3. Results and discussion

Fig. 1 shows the frequency dependence of the linear viscoelasticity functions for gel-like α-cellulose suspensions in castor oil media containing several ethyl celluloses with different molecular weights. This dependence is qualitatively similar to that found for other relatively concentrated colloidal suspensions like standard lubricating greases (Madiedo, Franco, Valencia, & Gallegos, 2000; Martín-Alfonso, Valencia, Sánchez, Franco, & Gallegos, 2007). As can be observed, G' is always higher than G'' in the whole frequency range studied. In addition, a pronounced plateau region of the mechanical spectrum is always noticed, as extensively described elsewhere for solid-like disperse systems (Batchelor, 1974; Delgado et al., 2005; Delgado et al., 2006a; Delgado, Valencia, Sánchez, Franco, & Gallegos, 2006b; Douglas, Lewis, & Spaull, 1971; Mewis & Spaull, 1976). This mechanical spectrum corresponds with the definition given by Almdal et al. (1993) for solid-like gels. However, both moduli show higher values than those found in standard lithium greases, being maxima for the oleogel containing ethyl cellulose with the highest molecular weight. Moreover, G' and G'' are not significantly influenced by ethyl cellulose molecular weight below a critical molecular weight (M_w < 70,000 g/mol). On the contrary, a significant increase in both SAOS functions, and a shift of the minimum in G'' to higher frequencies, are noticed when using ethyl cellulose with M_w values higher than the critical one. The above-mentioned increase in both linear viscoelasticity functions is quite similar in the low frequency range and, consequently, the relative elastic characteristics of these gel-like dispersions are not significantly affected, as can be observed in Fig. 1b where the loss tangent ($\tan\delta = G''/G'$) is plotted versus frequency. However, these differences increase with frequency. In this sense, formulations containing high-molecular weight ethyl celluloses show minimum loss tangent values at large frequencies.

Fig. 2a shows the mechanical spectra for formulations containing methylcellulose instead of α-cellulose. As can be observed, the evolution of G' and G'' with frequency is qualitatively similar than that found in oleogels containing α-cellulose/ethyl cellulose blends, although the values of both moduli are now significantly higher. As before, both SAOS functions are not influenced by ethyl cellulose molecular weight, below the same critical M_w value. Moreover, a significant increase in G' is observed for the oleogel containing ethyl cellulose with the highest molecular weight, yielding a slight decrease in the loss tangent (Fig. 2b). However, in this case, the frequency dependence of SAOS functions is not affected by ethyl cellulose molecular weight.

As previously reported (Sánchez et al., 2009), the mechanical spectra of the binary systems castor oil/α–cellulose and castor oil/methylcellulose are qualitatively similar to these discussed for ternary mixtures. The introduction of the ethyl cellulose in the formulation slightly increase the values of both G' and G'' without significant modification of the relative elastic characteristics, i.e. the values of the loss tangent. However, as shown in Fig. 3a, the ethyl cellulose significantly increases the oil viscosity (conferring also a shear thinning behaviour), which is essential to impart long-term physical stability to these gel-like dispersions. On the contrary to that found in the above-mentioned binary mixtures, no phase separation was visually detected at least during 8–9 months of ageing. As a consequence, the use of ethyl cellulose allows to reduce the other thickener content as well as to inhibit oil phase separation (oil bleeding), even when the sample is submitted to severe working conditions (Sánchez et al., 2009). This improvement in physical stability is not only due to the increasing oil viscosity but also to the viscoelastic properties of the castor oil/ethyl cellulose binary systems, which at the concentrations employed (2.6–2.9%, w/w) display a certain elastic-like character (see Fig. 3b). The mechanical spectra of these binary systems is similar to other non-aqueous ethyl cellulose solutions or weak gels (Heng, Chan, & Chow, 2005; Lizaso, Muñoz, & Santamaría, 1999), although the crossover between G' and G'' observed appears at higher frequencies in the data reported in the existing literature, depending on the solvent and ethyl cellulose concentration. In the ethyl cellulose/castor oil binary systems studied, this crossover between both SAOS functions is shifted to lower frequencies when the ethyl cel-

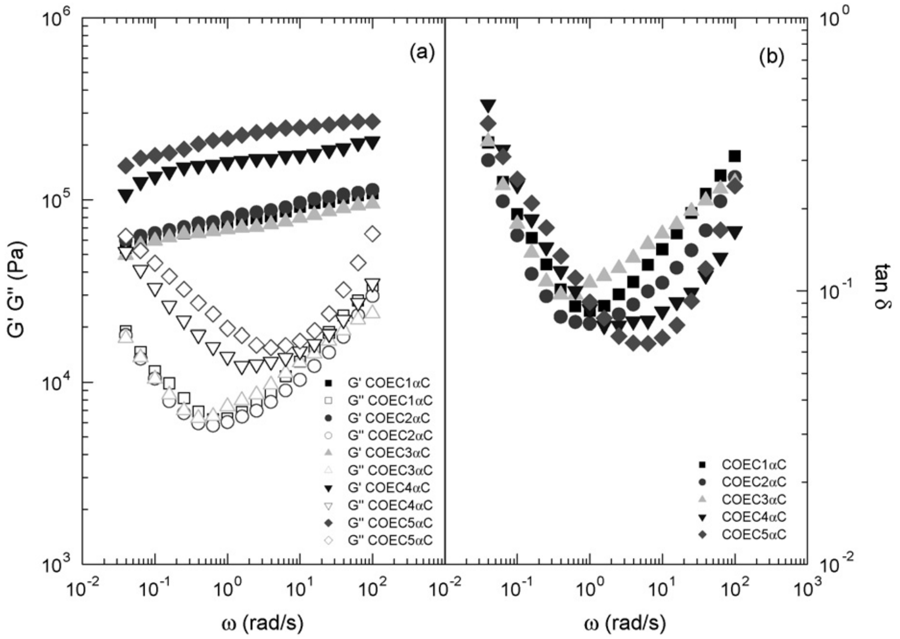

Fig. 1. Evolution of the storage and loss moduli (a) and the loss tangent (b) with frequency for oleogels formulated with blends of α-cellulose and ethyl cellulose with different number average molecular weight (M_w).

lulose molecular weight is increased. Moreover, G' and G'' values increase with the ethyl cellulose molecular weight, especially for $M_w > 53{,}000$ g/mol, which contributes to the behaviour above discussed for the ternary systems. This elastic character was mainly detected at temperatures below 60–65 °C, with values of the loss tangent of 0.3–3, depending on the frequency. Above this temperature, a significant increase in the loss tangent was observed (Fig. 3c).

Fig. 4 summarizes and compares the influence of the ethyl cellulose molecular weight on the plateau modulus of both α-cellulose and methylcellulose-based oleogels. As can be observed, the plateau modulus, G_N^0, a characteristic parameter of the plateau region in the mechanical spectrum (Baurngaertel, De Rosa, Machado, Masse, & Winter, 1992), increases above a critical ethyl cellulose molecular weight (M_w around 70,000 g/mol) and remains almost constant below it. Apart from the evolution of the SAOS functions with the ethyl cellulose molecular weight previously described for the binary systems (Fig. 3b), this behaviour may be also related to the classical evolution of viscosity with molecular weight found for polymer solutions (Ferry, 1980). As well-known, according to the Bueche theory, the viscosity of undiluted polymer solutions potentially increases with molecular weight but more rapidly above a certain molecular weight, which is illustrated in Fig. 3a where the viscosity, at 0.01 s^{-1}, is plotted versus the ethyl cellulose molecular weight for the ethyl cellulose/castor oil binary systems.

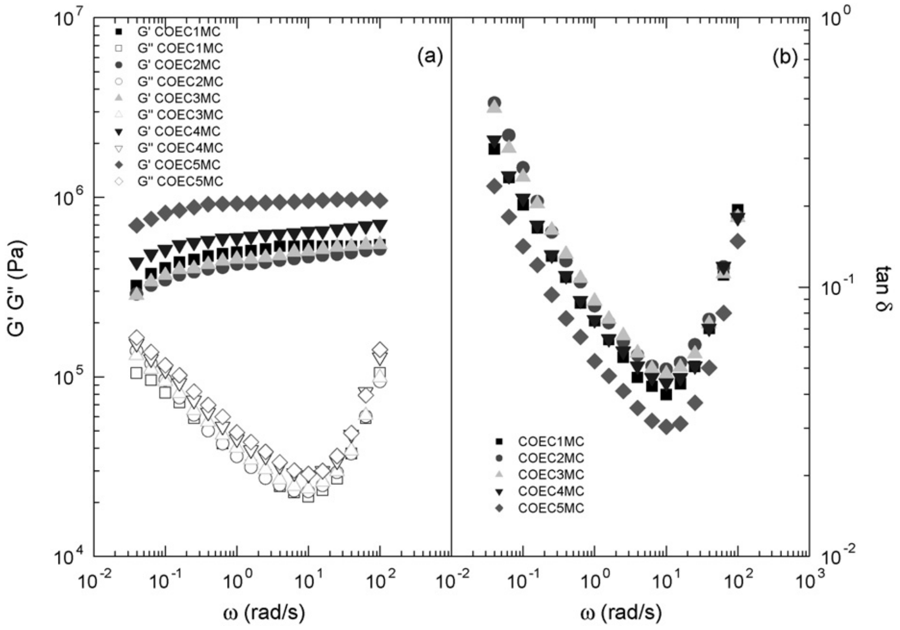

Fig. 2. Evolution of the storage and loss moduli (a) and the loss tangent (b) with frequency for oleogels formulated with blends of methylcellulose and ethyl cellulose with different number average molecular weight (M_w).

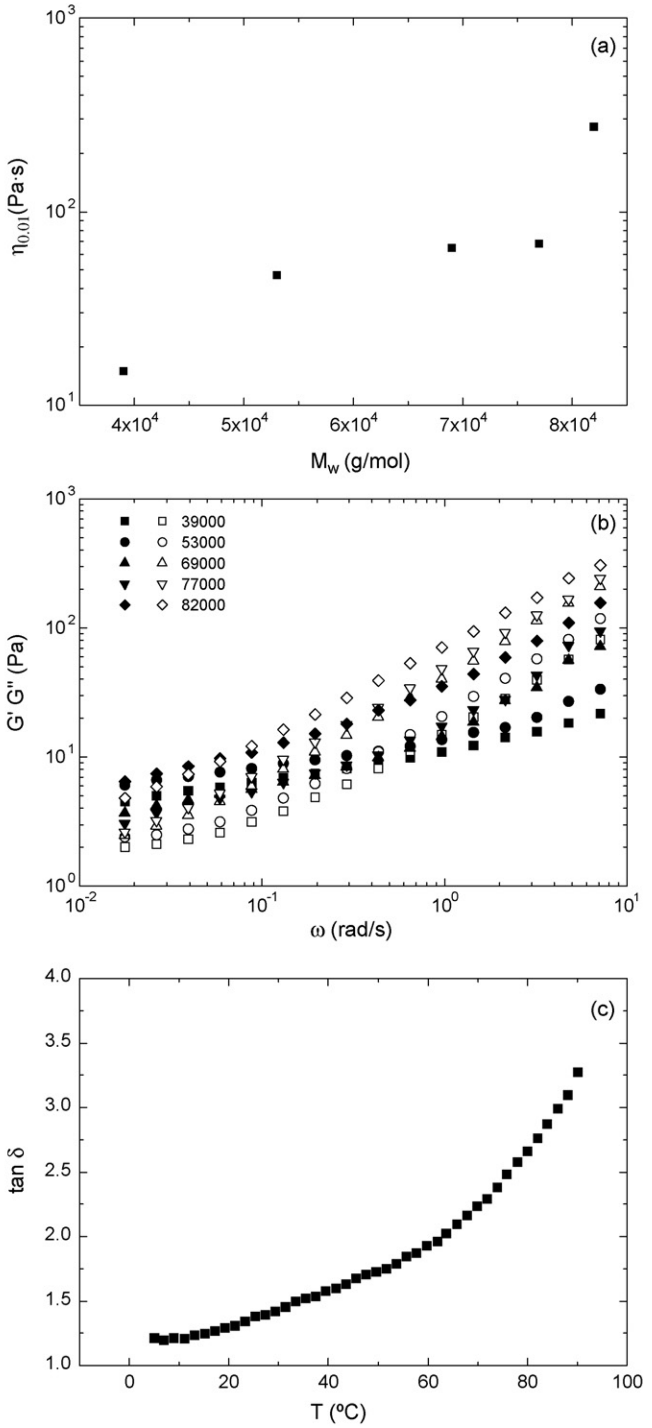

Fig. 3. Rheological characteristics of the ethyl cellulose/castor oil binary systems: (a) evolution of the apparent viscosity, at 0.01 s^{-1}, with ethyl cellulose molecular weight; (b) mechanical spectrum as a function of ethyl cellulose molecular weight (G' full symbols, G'' open symbols); (c) evolution of the loss tangent, at 0.1 rad/s, with temperature for a selected binary system (M_w = 69,000 g/mol).

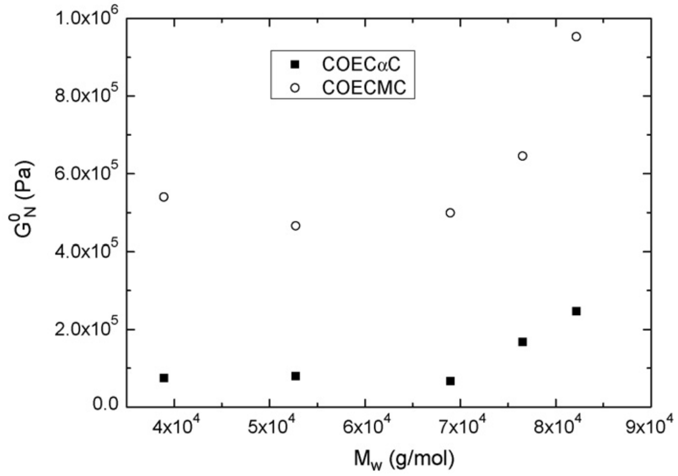

Fig. 4. Influence of the ethyl cellulose molecular weight on the plateau modulus, G_N^o, of both α-cellulose and methylcellulose-based oleogels.

Fig. 5 shows the evolution of SAOS functions with frequency, as a function of temperature, for a selected formulation (COEC5αC). As can be expected, the values of SAOS functions decrease with temperature in the whole frequency range studied, although a well developed plateau region is always noticed. On the other hand, the frequency dependence of both moduli is not qualitatively influenced by temperature, fact that is completely opposite to the behaviour reported for many standard greases (Delgado et al., 2006b). More surprisingly, the loss tangent is almost unaffected, which indicates that the relative elastic characteristics are not influenced by temperature either, in spite of the decrease in the relative elastic characteristics observed for the ethyl cellulose/castor oil binary systems at around 60 °C, Fig. 3c). Therefore, these oleogels microstructures seem to resist higher temperatures than metallic soap-based greases. For those standard greases, the elastic characteristics vanish above the soap melting point, i.e. around 200 °C in the case of lithium greases.

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:

$$G_N^o = A \cdot e^{(E_a/R)\cdot(1/T)} \tag{2}$$

where E_a is a parameter which evaluates the thermal dependence, 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). Eq. (2) fits the experimental plateau modulus values, in the whole temperature range studied, fairly well, as can be observed in Fig. 6 for a selected oleogel (COEC2MC). This is, once again, quite different to the behaviour of standard lithium greases. Thus, two different Arrhenius-type equations are necessary to fit the evolution of standard lubricating grease plateau modulus with temperature, being the thermal dependence of SAOS functions much more dramatic above a critical temperature (Delgado et al., 2006b). Table 4 gathers E_a values, obtained from Eq. (2), for all gel-like dispersions studied. As can be seen, α-cellulose suspensions display higher values of E_a than gel-like dispersions manufactured with methylcellulose. Moreover, these E_a values are higher than those obtained for standard lithium greases in the

Table 4
Activation energy values, from Eq. (2), for the different oleogels studied.

Sample	E_a (kJ/mol)
COEC1αC	5.0
COEC2αC	5.8
COEC3αC	6.0
COEC4αC	5.1
COEC5αC	5.3
COEC1MC	3.9
COEC2MC	4.8
COEC3MC	3.5
COEC4MC	4.0
COEC5MC	4.1

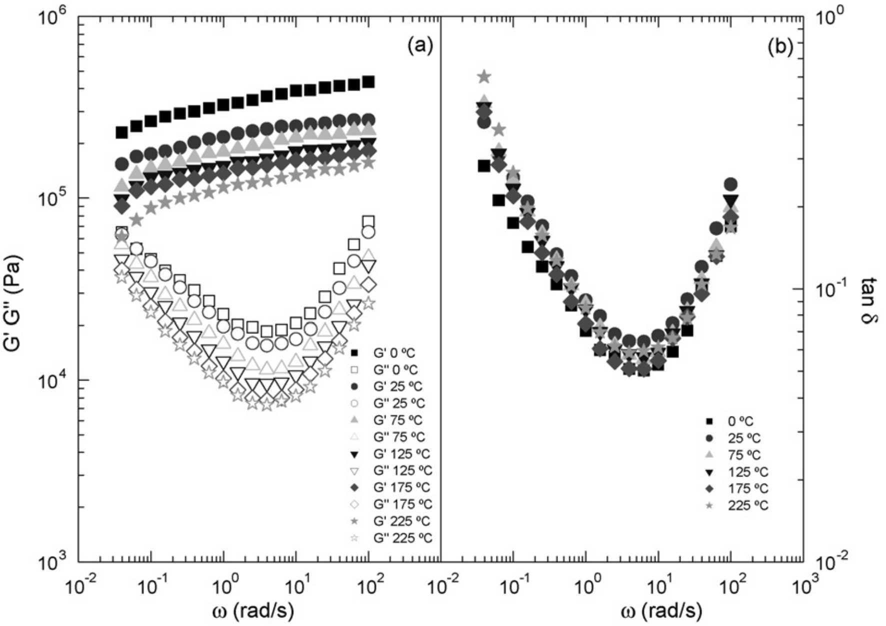

Fig. 5. Evolution of the storage and loss moduli (a) and the loss tangent (b) with frequency for a selected oleogel, COEC5αC, at different temperatures.

low-temperature range (1–2 kJ/mol), but much lower than those found in the high-temperature range (18–20 kJ/mol) (Delgado et al., 2006b).

One of the technical parameters more often used by lubricating grease manufacturers and customers is grease mechanical stability, obtained from penetration tests before and after working the sample. In this study, samples were worked in a roll stability tester. Mechanically stable greases display penetration increments (before and after working the sample) close to zero. Table 5 shows worked and unworked penetration values, and their differences (penetration variations), for of all the oleogels manufactured in this study. Furthermore, penetration values for different lithium soap-based lubricating greases containing different base oil (paraffinic, naphtenic and castor oil) have been also included. In order to classify the different types of samples studied, penetration values of unworked samples were converted to NLGI grades, according to the ASTM D 217 standard. In general, α-cellulose-based oleogels show poor mechanical stability, with penetration increments much higher than those obtained with the lithium greases selected as benchmarks. Specifically, α-cellulose-containing oleogels 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 value, yielding the worst mechanical stability.

On the other hand, both unworked and worked penetrations values clearly decrease by increasing ethyl cellulose molecular weight for methylcellulose-based oleogels. Moreover, the penetration values are generally lower than those found in oleogels with α-cellulose, yielding higher NLGI grades, similar to those found for lithium greases. Most remarkable is the improved mechanical stability shown by these oleogels, particularly those including ethyl cellulose with high-molecular weight. Thus, the use of methylcellulose and high-molecular weight-ethyl cellulose blends in these oleogel formulations provides a mechanical stability comparable to that obtained with standard lithium lubricating greases.

Table 5 also shows leakage tendency values of oleogels in wheel bearings (ASTM D 1263). As can be seen, a very high level of leakage was always obtained, independently of both nature of the cellulosic derivative and ethyl cellulose molecular weight. This high level of leakage is related to the rather high-temperature (105 °C) at which these standard tests are carried out. As it was previously discussed, an important softening of the binary systems, associated to a significant decrease in the relative elastic characteristics, was detected at around 60 °C. Above this temperature, the viscosity of the oily phase is significantly reduced and, therefore, the leakage is favoured. However, it is worth mentioning that the same tests performed at room temperature provide very similar leakage values to those shown by lithium greases (1.8 ± 0.5%).

Table 5
Penetration and leakage values for oleogels, model lithium soap/castor oil grease, and standard lubricating greases.

Sample	Unworked penetration (dmm)	NLGI grade	Worked penetration (dmm)	Penetration variation (dmm)	Leakage (%)
COEC1αC	384	0	474	90	40.4 ± 0.7
COEC2αC	377	0	470	94	
COEC3αC	380	0	467	86	
COEC4αC	377	0	485	109	
COEC5αC	369	0	504	135	
COEC1MC	380	0	392	12	30.9 ± 1.0
COEC2MC	369	0	377	8	
COEC3MC	324	1	332	8	
COEC4MC	294	2	298	4	
COEC5MC	275	2	279	4	
COLi	242	3	260	18	0.4
Standard paraffinic oil-based grease	303	1–2	305	2	1.2
Standard naphtenic oil-based grease	274	2	289	15	0.8

Table 6
Characteristic decomposition temperatures, from TGA measurements, for oleogels and lubricating grease benchmarks.

Sample	Atmosphere	T_{range} (°C)		T_{max} (°C)
		T_{onset} (°C)	T_{final} (°C)	
COECαC	N_2	352.0 ± 1.4	417.2 ± 1.1	391.6 ± 2.4
	O_2	322.4 ± 2.7	415.0 ± 0.7	369.0 ± 3.1
COECMC	N_2	345.4 ± 1.8	396.4 ± 1.0	374.3 ± 2.4
	O_2	338.2 ± 1.1	394.4 ± 1.5	365.4 ± 2.3
COLi	N_2	329.2	403.0	362.4
	O_2	321.5	–	357.2
Standard paraffinic oil-based grease	N_2	188.3	–	245.4
	O_2	181.6	–	245.1

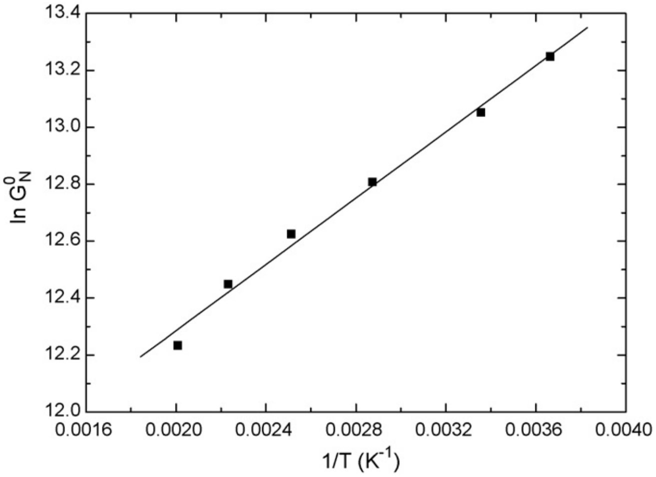

Fig. 6. Evolution of the plateau modulus (square symbols) with temperature, and Arrhenius' fitting (solid line), for a selected oleogel (COEC2MC).

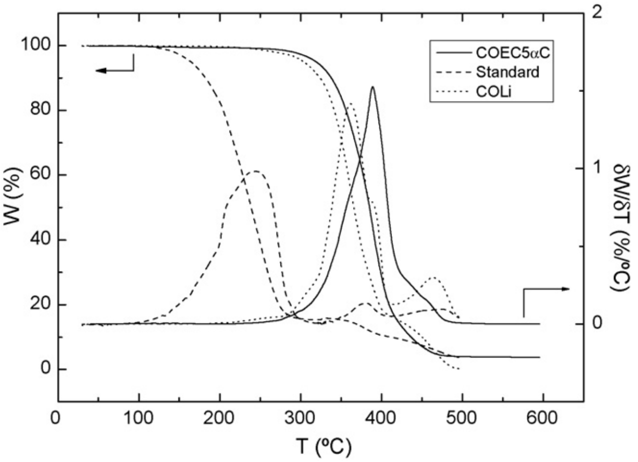

Fig. 7. TGA thermograms for a selected oleogel, a standard lubricating grease and a partially-biodegradable material.

In addition to mechanical stability, thermal resistance is another important issue for biolubricant formulations. Fig. 7 shows themogravimetric analysis curves for a selected cellulosic derivative-based oleogel, as compared with two benchmarks, a standard paraffinic oil-based lithium grease and a partially-biodegradable grease (based on lithium soap and castor oil). In general, thermal decomposition takes place in just one main single stage, which is almost identical for all the oleogels studied. As can be observed, castor oil-based formulations can resist much higher temperatures, without losing a significant amount of mass, than the paraffinic-based grease. Thus, the main factor affecting TGA response is the volatility of the base oil used in these formulations. However, substitution of lithium soap for cellulosic derivatives also delays the onset temperature for thermal decomposition (T_{onset}) and, in general, the whole decomposition range. Table 6 shows the most relevant temperatures obtained from the TGA analysis, using both nitrogen and oxygen atmospheres, for all the oleogels studied and for the formulations taken as references. T_{onset} was determined from the interception between the slope of the first region, where the sample weight is approximately constant, and the slope of the region where sample weight loss rate is maximum, whereas T_{max} is the temperature which corresponds to the maximum of the weight loss derivative function. Oleogel thermal stability is not influenced by ethyl cellulose molecular weight. On the contrary, it is clearly affected by the nature of the second cellulose derivative, employed as thickener. In this sense, Table 6 shows the mean values of the above-mentioned characteristic temperatures, and the corresponding standard deviations, for oleogels containing α-cellulose or methylcellulose. It is apparent that the formulation containing α-cellulose shows the best thermal stability when a nitrogen atmosphere is used. On the contrary, this oleogel displays T_{onset} values lower than the methylcellulose-based formulation when an oxygen atmosphere is used, although a wider decomposition temperature range, that is, higher T_{final}.

4. Conclusions

The influence that ethyl cellulose molecular weight exerts on the final properties of oleogels formulated with castor oil and α-cellulose/ethyl cellulose, or methylcellulose/ethyl cellulose blends, has been investigated. Addition of ethyl cellulose, with different molecular weights, yields, in some cases, oleogel formulations with rheological, thermal and mechanical properties suitable for potential lubricating applications. From a rheological point of view, oleogels SAOS functions are influenced by ethyl cellulose molecular weight only above a critical value ($M_w < 70{,}000$ g/mol). Addition of low and medium molecular weight ethyl cellulose does not exert a significant influence on SAOS functions. Moreover, temperature does not influence the relative elastic characteristics of these oleogels, nor their qualitative dependence on frequency. Oleogels containing methylcellulose/ethyl cellulose blends display improved mechanical stability, which is enhanced by increasing ethyl cellulose molecular weight, and quite similar to that found for standard lithium greases. However, cellulosic derivatives-based oleogels show much higher high-temperature leakage tendency than that shown by lithium greases, which is related to the sol–gel transition temperature of ethyl cellulose in the oil medium. On the contrary, the oleogel formulations studied display much higher decomposition temperatures than standard lubricating greases, independently of ethyl cellulose molecular weight.

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