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Use of chitin, chitosan and acylated derivatives as thickener agents of vegetable oils for bio-lubricant applications

R. Sánchez, G.B. Stringari, J.M. Franco*, C. Valencia, C. Gallegos

Departamento de Ingeniería Química, Facultad de Ciencias Experimentales, Campus de "El Carmen", Universidad de Huelva, 21071 Huelva, Spain

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ABSTRACT

This work deals with the development of new gel-like formulations prepared from natural resources, which could be potentially applicable as environmentally friendly lubricating greases. In particular, the use of chitin, chitosan and acylated derivatives as thickener agents of vegetable oils, which may represent an alternative to the traditional metallic soaps or polyurea derivatives, was explored. Biopolymers used to obtain oleogels were chemically and thermally characterized. Oleogels thermal and rheological behaviours were studied by means of TGA and DSC tests, and linear viscoelasticity measurements, respectively. Moreover, some lubricant performance properties were evaluated. The evolution of linear viscoelasticity functions with frequency was very similar to that found for standard lubricating greases. In general, linear viscoelasticity functions increased with biopolymer concentration, whilst they decreased when acylated chitosan or soybean oil were used in the oleogel formulation. The use of acylated chitosan with a degree of acylation of around 0.3 provides oleogels with very similar rheological properties than those shown by traditional lubricating greases, as a consequence of reducing the biopolymer polarity. However, chitin and chitosan-based oleogels show higher thermal stabilities than formulations containing acylated chitosan. In general, oleogel samples studied exhibited values of the friction coefficient comparable to those found for standard lithium greases. However, most of these oleogels generally display a quite poor mechanical stability in rolling elements.

1. Introduction

Lubricating greases are generally described as structured colloidal suspensions where a solid thickener and/or gelling agent is dispersed in a lubricating oil (Hamnelid, 2000). Some additional components, called additives, are normally included, in order to improve specific properties and functions. The main difference between lubricating greases and other lubricants is their characteristic rheological behaviour, frequently referred as consistency in the lubricant industry, which results from the addition of the thickener. Suitable rheological properties make possible the use of lubricating greases in applications where liquids do not work properly, acting as a solid or semisolid body at low stresses. Thus, for instance, fluctuations with temperature, loads, vibrations and surrounding environment conditions, within reasonable limits, can be all handled by using this type of product. Moreover, the matrix of the bulk lubricating grease can absorb contaminants, such as particles and water, in relatively large amounts, without reduction in its lubricating properties. This is due to the fact that only a limited part of the lubricating grease is used for actual lubrication, the remaining acting as a seal (Hamnelid, 2000). As extensively reported, the rheological behaviour and related functional properties of a lubricating grease depend on both its composition and the manufacturing process used (Delgado, Sánchez, Valencia, Franco, & Gallegos, 2005; Delgado, Valencia, Sánchez, Franco, & Gallegos, 2006a; Franco, Delgado, Valencia, Sánchez, & Gallegos, 2005). The most common composition of lubricating greases is a mineral oil thickened with metallic soaps, silica and bentonite particles or polyurea derivatives although it may also contain additives, such as anti-oxidants and anti-corrosion.

Nowadays, it is well-known that there is an increasing interest in the use of natural components in a wide variety of manufactured products, due to the 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 (Lea, 2002). In this sense, a new market based on eco-friendly products is developing quite fast, where consumers are well disposed to test new products or even pay higher prices if they receive an alternative material with reduced negative effects on the environment. Concerning the impact that lubricants exert on the environment, it is estimated that, every year, more than 10 million tons of engine, industrial and hydraulic oils are returned into the environment (Bartz, 1998). This is a very problematic situation from an environmental point of view, since even small amounts

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* Corresponding author. Tel.: +34 959219995; fax: +34 959219983.
E-mail address: franco@uhu.es (J.M. Franco).

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of these products, which are accidentally spilled on ground and water, can inhibit the growth of trees and can be toxic to aquatic life (Wilson, 1998).

Vegetable oils are promising candidates to be used as eco-friendly lubricants, presenting good lubricity, ability for adhering metal surfaces, weak viscosity-temperature dependence, non-toxicity, and high biodegradability. Although raw vegetable oils present some shortcomings, like poor oxidation stability, deficient low temperature flow properties and small range of viscosities, previous studies demonstrated that these properties can be improved by using some additives (Erhan, Sharma, & Perez, 2006; Quinchia, Delgado, Valencia, Franco, & Gallegos, 2009). However, developing lubricating greases based on 100% biodegradable raw materials is a much more complicated task, due to the difficulty of the substitution of the thickener agents traditionally used (metallic soaps, phyllosilicates or polyurea compounds) by other environmentally friendly additives. Thus, a bio-thickener should convey to the oleogel similar or improved rheological characteristics, and thermal and mechanical stabilities to those provided by traditional metallic soaps.

Previous research carried out by some of the authors reported the use of sorbitan monostearate as gelling agent in the formulation of bio-lubricating greases. Some oleogels containing this thickener showed viscoelastic properties and tribological characteristics similar to those found with standard lithium greases. However, some weaknesses were observed regarding their mechanical stability and properties thermal dependence (Sánchez, Franco, Delgado, Valencia, & Gallegos, 2008). On the contrary, an improved thermal resistance was found for formulations thickened with cellulose derivatives (even better than that found for standard lubricating greases), as well as satisfactory mechanical and physical stabilities, especially in the case of oleogels formulated with castor oil and blends of ethyl and methyl cellulose (Sánchez, Franco, Delgado, Valencia, & Gallegos, 2009, 2011). However, in these cases, suitable mechanical and physical stabilities were linked to values of the linear viscoelastic functions much higher than those found for standard greases. In this sense, it is necessary to investigate the performance of other natural thickeners, aiming to develop new biogreases with the whole set of relevant properties matching those of the benchmark. Finding this new biodegradable thickener agent, obtained from natural resources, may create a new market niche with interesting perspectives for the future (Fessenbecker, 2003).

In addition to cellulose derivatives, chitin and its derivatives are another interesting group of biopolymers that could be used as potential thickeners for biolubricant applications. Chitin is a natural polysaccharide, synthesized by a large number of living organisms, mostly found in the shell of crustacean, the cuticles of insects, and the cell walls of fungi (Knorr, 1984). Chitin is considered the most abundant biopolymer in nature after cellulose. When the degree of deacetylation of chitin reaches about 50%, it becomes soluble in aqueous acidic media and is called chitosan (Rinaudo, 2006). In this work, the potential use of chitin, chitosan and some other acylated derivatives, as bio-thickener agents to formulate stable dispersions in vegetable oils, is explored. Rheological and thermogravimetric characterizations, as well as evaluation of some lubricant performance properties (friction coefficient and mechanical stability) were carried out, in order to investigate the potential applicability of these gel-like dispersions as biodegradable lubricating greases.

2. Materials and methods

2.1. Materials

Castor (Guinama, Spain) and soybean (kindly supplied by Fresenius Kabi, Sweden) oils were used as base oils for oleogel formulations studied. Moreover, three biopolymers were evaluated as potential thickeners or gelling agents: chitin (CC), purchased from Qingdao Fraken (China), and low (LMC) and medium (MMC) molecular weight chitosan (Sigma–Aldrich, Germany). The average molecular weight and degree of deacetylation (DD) of the original biopolymers are shown in Table 1. In addition, acylated chitosan samples (synthesis procedure described below) were also tested. All other common reagents and solvents employed were purchased from Sigma–Aldrich.

Table 1
Mean molecular weight and degree of deacetylation (DD) of the chitin and chitosan biopolymers used.

Thickener	Mean molecular weight (g/mol)[a]	DD (%)[b]	DD (%)[c]
CC	5.4×10^5	–	7.3
LMC	3.9×10^{5}[d]	83.4[d]	87.6
MMC	5.6×10^{5}[d]	83.1[d]	82.1

[a] Determined by viscometric methods.
[b] Determined using the titration method.
[c] Determined from IR analysis.
[d] Values taken from Takahashi et al. (2005).

Standard lithium 12-hydroxystearate lubricating greases (14 and 20% lithium soap, NLGI grade 1–2) 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 these traditional lubricating greases, using the methodology reported elsewhere (Delgado et al., 2005, 2006a).

2.2. Acylation of chitosan

The acylation reaction of chitosan was basically performed following the method described by Ma, Yang, Kennedy, and Nie (2009). Chitosan (24.0 g) was soaked in a mixed solvent of triethylamine (250 mL) and acetone (250 mL), for 24 h at 50 °C, and then cooled and stirred, for 1 h at 0 °C. Stearoyl chloride (48 g) dissolved in acetone (300 mL) was added drop wise into the mixed solution within 1 h and, then, the temperature was gradually increased to 90 °C during 4 h, and maintained for 1 h more. Afterwards, the solution was cooled down to room temperature without stirring and, finally, grounded. This synthesis was performed using medium- and low-molecular weight-chitosan, resulting two different products, which are referred as A2MMC and A2LMC, respectively. The same procedure was followed when the stearoyl chloride/chitosan mass ratio (3:1) was changed. In this case, the resulting products are referred as A3MMC and A3LMC for the medium- and low-molecular weight-chitosan, respectively. The determination of the average substitution degree achieved was carried out according to the method described by Klemm, Philipp, Heinze, and Wagenknecht (1998), expressed over the maximum possible substitution of the monomer, i.e. from 0 to 4 (see Table 2).

Table 2
Degree of substitution, melting temperature and fusion enthalpy data of the acylated chitosan samples obtained in this study.

Biopolymer	Degree of substitution	1st peak		2nd peak	
		T_m (°C)	ΔH_f (J/g)	T_m (°C)	ΔH_f (J/g)
A2MMC	0.3	43	18	64/74	40
A3MMC	0.7	40	13	65/73	44
A2LMC	0.8	39	12	65/72	64
A3LMC	1.0	40	11	65/73	67

Table 3
Compositions of the oleogel formulations studied.

Thickener agent	Concentration (%, w/w)	Vegetable oil (up to 100%, w/w)	Code applied
CC	19	Castor	CC-19
CC	21	Castor	CC-21
CC	21	Soybean	CC-21-S
CC	23	Castor	CC-23
MMC	23	Castor	MMC-23
MMC	25	Castor	MMC-25
MMC	27	Castor	MMC-27
MMC	27	Soybean	MMC-27-S
LMC	39	Castor	LMC-39
LMC	39	Soybean	LMC-39-S
A2MMC	35	Castor	A2MMC-35
A3MMC	35	Castor	A3MMC-35
A2LMC	35	Castor	A2LMC-35
A3LMC	35	Castor	A3LMC-35

2.3. *Processing of oleogels*

Processing of oleogel samples was performed in an open vessel, using a controlled-rotational speed mixer (60 rpm), equipped with a helical ribbon impeller to disperse the different biopolymers. Thickener concentrations were previously optimized to provide physically stable oleogels, i.e. without significant oil bleeding. Batches of 220 g were prepared for each formulation investigated (see Table 3). Samples were heated, up to 85–90 °C, whilst dispersing the biopolymer, in order to decrease its viscosity and improve mixing. The mixing process was maintained during 1 h. Finally, oleogel cooling down to room temperature was carried out by external natural convection, under continuous internal stirring, in the same heating device.

2.4. *Thermogravimetric analysis (TGA)*

Measurements of mass losses versus temperature were performed using a Thermogravimetric analyzer, model Q-50 (TA Instrument Waters, USA), under N_2 purge. Typically, 5–10 mg of sample were placed on a Pt pan, and heated from 30 °C to 600 °C, at 10 °C/min.

2.5. *Differential scanning calorimetry (DSC)*

DSC measurements were performed with a Q-100 TA instrument, using 5–10 mg samples sealed in hermetic aluminium pans, and heated from −80 up to 200 °C. Then, a second heating ramp was performed, in order to eliminate the thermal-history and residual moisture. In all cases, a heating rate of 10 °C/min was applied, and the samples were purged with N_2, at a flow rate of 50 mL/min.

2.6. *Fourier transform infrared spectroscopy (FTIR)*

FTIR spectra were obtained with a Digilab FTS3500ARX (Varian) apparatus. Biopolymer samples were prepared as KBr pellets and placed into an appropriate sample holder. The spectra were obtained in a wavenumber range of 400–4000 cm^{-1}, at 4 cm^{-1} resolution, in the transmission mode.

2.7. *Microscopy observations*

The morphological characterization of oleogels was carried out by means of optical microscopy using an Olympus microscope, BX51 model (Japan), equipped with a digital camera and thermostatic circulator. Micrographs were obtained at 25 °C.

2.8. *Rheological characterization*

Rheological characterization was carried out with two controlled-stress rheometers, Rheoscope (ThermoHaake, Germany) and Gemini (Bohlin, UK). Small-amplitude oscillatory shear (SAOS) tests were performed inside the linear viscoelastic region, using plate-plate geometries (35 mm diameter and 25 mm diameter, respectively, and 1 mm gap), in a frequency range of 10^{-2} to 10^{2} rad/s, at 5, 25, 50, 100 and 130 °C. At least two replicates of each test were performed on fresh samples.

2.9. *Penetration and mechanical stability tests*

Both unworked and worked penetration indexes were determined according to the ASTM D1403 standard, by 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, following the ASTM D217 standard. Classical consistency NLGI grade was established according to these penetration values (NLGI, 1994). The same samples were worked during 2 h in a Roll Stability Tester, model 19400-3 (Stanhope-Seta, UK), as indicated in the ASTM D1831 standard and, then, penetration measurements were carried out, once again, after this rolling test. Sample mechanical stability was then calculated as the difference between worked and unworked penetration values. At least three replicates of penetration measurements were performed.

2.10. *Tribological tests*

Tribological tests were performed in a Nanotribometer (CSM Instruments, Switzerland) with a classical ball-on-disc geometrical coupling, using a ball diameter of 1.5 mm, and working in the rotational mode, by selecting a normal load of 50 mN, a track radius of 7 mm, and a linear speed of 10 mm/s. The material combination for these series of measurements was a sapphire ball on a sapphire plate, both with a maximum roughness of 1 μm. The friction coefficient was continuously measured, during 15 min, as the ratio between the resulting friction and the normal forces applied. Forces were determined by means of optically detecting the displacement of a cantilever. Frictional force was measured with a resolution of 0.01 mN. In all cases, a deflector had to be applied to re-spread the grease after each revolution. Three replicates of the friction coefficient were done, at room temperature, and the average value calculated.

3. Results and discussion

3.1. *Thermal and spectroscopic characterization of biopolymers*

The different chitin derivatives employed as thickeners were thermally characterized by means of DSC and TGA techniques. Fig. 1 shows the DSC curves for selected non-acylated and acylated chitosan samples. As can be observed, samples MMC and LMC do not show any melting or glass transition event in the temperature range from −80 °C to 200 °C. In this sense, the rheological properties of the final products thickened by these biopolymers should not dramatically change with temperature. On the other hand, the acylated biopolymers heat flow curves display two main peaks, which can be related to acylated chitosan structures with different degrees of substitution and, consequently, two different melting temperatures. Table 2 shows the melting temperatures found for all the acylated chitosan samples studied. In general, the melting temperatures are the same for all the samples, excepting for sample A2MMC, with lower degree of substitution, which displays a first

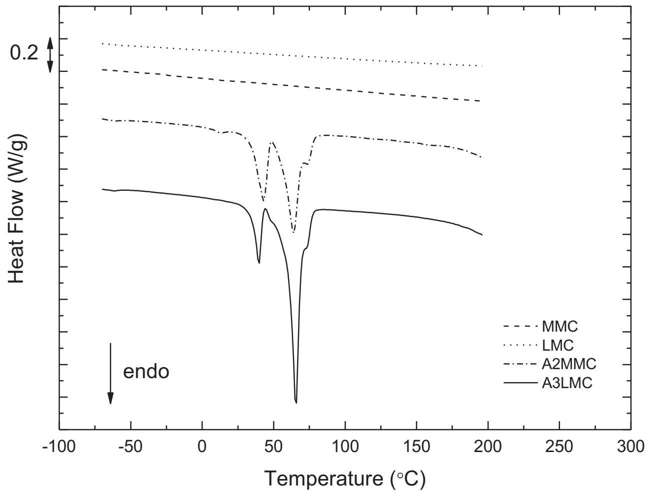

Fig. 1. DSC heat flow curves for MMC, LMC, A2MMC and A3LMC samples.

melting peak slightly shifted to higher temperatures. In this particular case, the fusion enthalpy (ΔH_f) is also slightly higher than those found for all the remaining samples studied (see Table 2), which indicates a larger proportion of the less acylated component, associated to this first melting peak. However, the fusion enthalpy (ΔH_f) corresponding to the second peak clearly decreases with chitosan molecular weight and increases with the substitution degree (see Table 2). This fact supports the X-ray diffraction results previously reported (Ma et al., 2009), which suggest that the crystallinity of acylated chitosan increases with the number of long aliphatic chain introduced. The acylated structures have been also investigated using FTIR techniques. Fig. 2 displays selected FTIR spectra for CC, MMC and A2MMC samples, respectively. As expected (Guinesi & Cavalheiro, 2006), chitin and chitosan FTIR spectra are very similar (see Fig. 2a and b), mainly differing in the intensity of the absorption bands at around 1655 cm^{-1}, corresponding to N-acetyl groups, and 3440 cm^{-1}, attributed to the inter- and intra-molecular hydrogen bonding of both –NH$_2$ and –OH stretching vibration, respectively. The different intensities of both peaks can be used to determine the degree of deacetylation (DD), as previously reported (Baxter, Dillon, Taylor, & Roberts, 1992; Guinesi & Cavalheiro, 2006; Lee, Ha, & Park, 1995). DD values, obtained from FTIR analysis, are compared in Table 1 with those found in the literature using the titration method (Takahashi, Imai, & Suzuki, 2005). In addition to this, the broad band at around 3440 cm^{-1} is clearly reduced in the acylated compound (Ma et al., 2009) and a new peak appears at 1704 cm^{-1}, assigned to the C=O of –N(COR)$_2$ and –OCOR groups, as a consequence of the acylation reaction between stearoyl chloride and –NH$_2$ or –OH groups of chitosan. Other new significant peaks, at 2920 and 2850 cm^{-1} (see Fig. 2c), assigned to the asymmetrical and symmetrical bending vibrations of methylene groups, confirm the insertion of long aliphatic chains in the chitosan molecular structure.

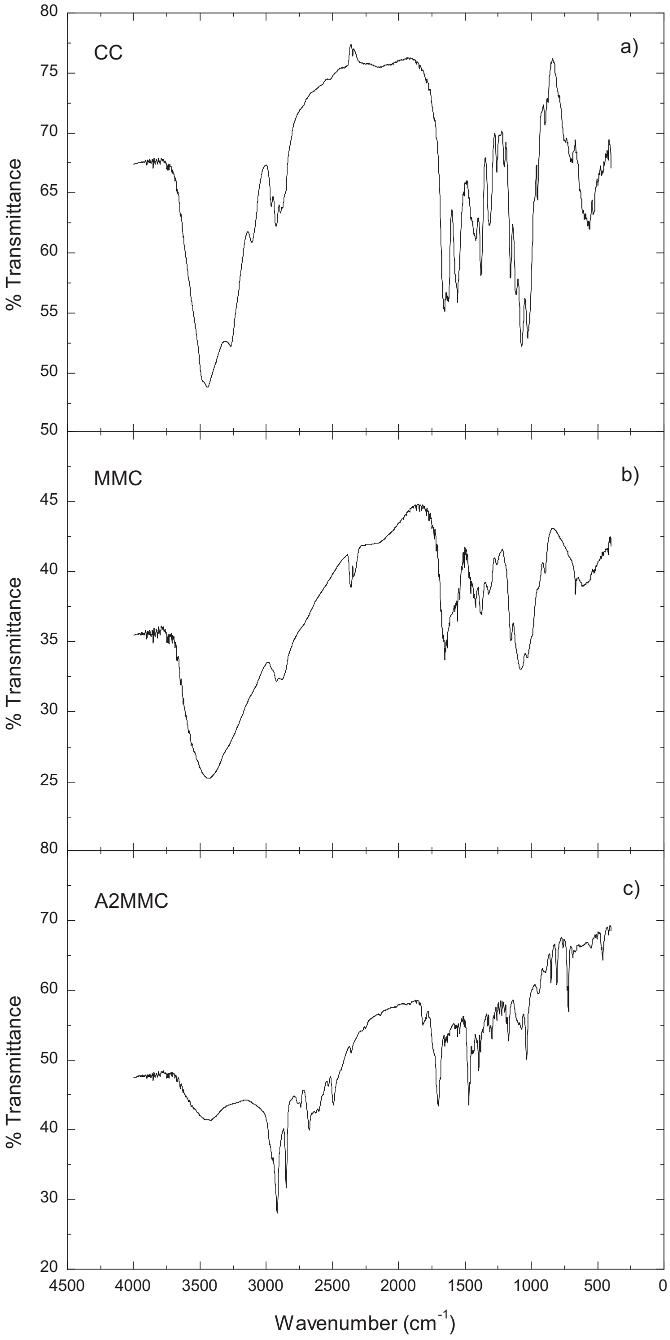

Fig. 2. Selected IR spectra for CC, MMC and A2MMC samples.

Fig. 3a shows selected thermogravimetric curves (weight loss vs. temperature and its derivative function) for some of the biopolymers studied. Table 4 gathers the main characteristic parameters derived from this analysis (estimated as indicated elsewhere Sánchez et al., 2009), and related to the thermal stability of the biopolymers used as thickeners. As can be seen, in general, biopolymer thermal decomposition occurs in one single stage, although the temperature decomposition range (T_{final}–T_{onset}) is much wider for the acylated chitosan samples, as a consequence of the different degrees of acylation achieved. The highest thermal stability corresponds to the chitin sample, showing values of T_{onset} and temperature for the maximum decomposition rate, T_{max}, much higher than chitosan and acylated chitosan samples, which is attributed to the decomposition of the chitin acetoamide groups (Guinesi & Cavalheiro, 2006). On the contrary, the acylated chitosan samples present the lowest thermal stability, showing T_{onset} of around 190 °C, whilst LMC and MMC samples show very simi-

Table 4
TGA characteristic parameters for some of the biodegradable thickeners studied.

	T_{onset} (°C)	T_{max} (°C)	T_{final} (°C)	Residue (%)
CC	336	383	398	26.4
MMC	284	301	330	27.7
LMC	280	298	328	30.8
A2MMC	190	241	275	16.4
A3LMC	198	246	269	7.0

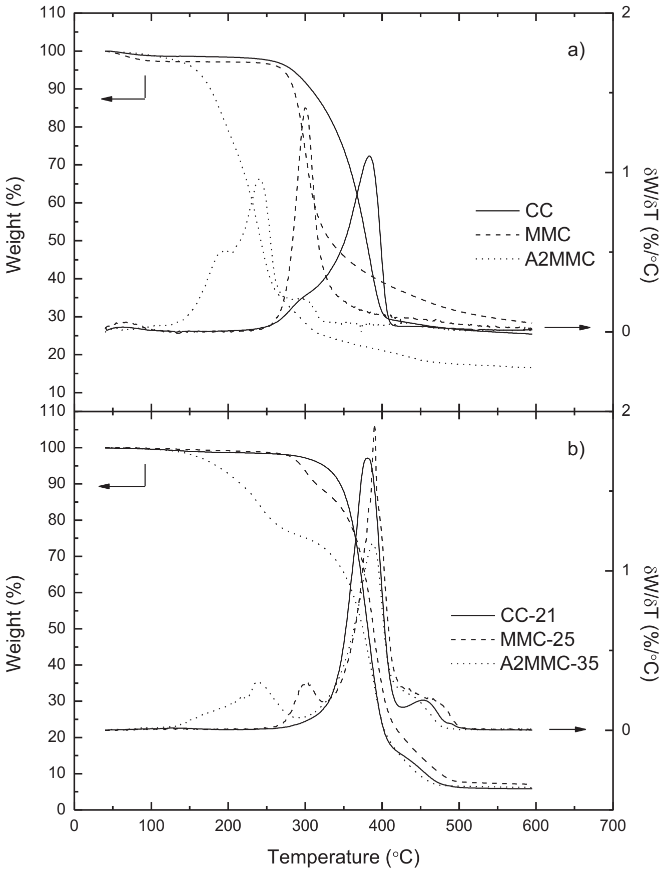

Fig. 3. TGA thermograms for (a) selected biopolymers and (b) some of their corresponding oleogel formulations. Weight loss vs. temperature plot and its derivative function.

lar characteristic degradation temperatures (Table 4), associated to their higher amine groups contents (Guinesi & Cavalheiro, 2006). These results are in agreement with those found by Zong, Kimura, Takahashi, and Yamane (2000), who concluded that the thermal stability of acylated chitosans was lower than that found for chitosan. These authors also found that the decomposition temperature increased with the length of the aliphatic chain inserted in the chitosan molecule, being, for instance, around 255 °C for the lauroyl-substituted chitosan, which is slightly lower than that obtained in this work for stearoyl-substituted chitosans. However, the maximum decomposition temperature found for acylated chitosan is much lower than those obtained by Ma et al. (2009), who reported values even higher than chitosan $T_{\max}$ values.

3.2. *Thermogravimetric analysis of oleogel formulations*

As can be observed in Fig. 3b, thermal decomposition of oleogel samples containing chitin, chitosan, or acylated derivatives occurs in two main stages. The first one corresponds to the decomposition of the biopolymer (as can be deduced from the characteristic temperatures shown in Tables 4 and 5), whilst the second one, much more remarkable, is associated to the thermal degradation of the castor oil. In the case of the chitin-based oleogel, thermal decompositions of both biopolymer and castor oil occur at similar temperatures and, consequently, only one main thermal event is clearly detected, i.e. one main peak in the weight loss vs. temperature derivative function. The characteristic temperatures obtained from TGA are listed in Table 5 for selected oleogel samples, which are potentially applicable as bio-lubricating greases. As expected, oleogel formulations prepared with LMC and MMC chitosan samples show almost identical thermal stabilities, otherwise much higher than formulations containing acylated chitosans as thickener (see Table 5). Nevertheless, the chitin-based oleogel displays the highest T_{onset} and $T_{\max}$ values and, therefore, can be considered the most thermo-resistant formulation.

Table 5 also includes characteristics parameters for thermal decomposition of two standard lithium greases, manufactured with paraffinic and naphthenic oils, respectively, which occurs in one main single stage. As can be observed, chitin and chitosan-based dispersions tolerate much higher temperatures without losing a significant amount of mass (T_{onset}) than mineral oil-based greases. Besides this, the characteristic temperatures associated to the first thermal decomposition event of acylated chitosan-based oleogels are very similar to those found for standard lithium greases (Martín-Alfonso, Valencia, Sánchez, Franco, & Gallegos, 2009).

3.3. *Rheological characterization of oleogel formulations*

Figs. 4 and 5 show the mechanical spectra, obtained from SAOS measurements inside the linear viscoelastic range, for chitin- and chitosan-based gel-like dispersions, respectively. As can be observed, the so called “plateau” region of the mechanical spectrum is always noticed. In this region, the storage modulus, G', is always higher than the loss modulus, G'', in the whole frequency range studied. G' slightly increases with frequency, whilst G'' displays a clear minimum. This mechanical spectrum corresponds with the definition given by Almdal, Dyre, Hvidt, and Kramer (1993), for soft solid-like gels. These gel-like characteristics, achieved via intermolecular hydrogen bonding and dipole–dipole interactions involving hydroxyl and amine groups of the chitin and chitosan chains and polarized groups of triglyceride molecules, especially the carbonyl group, are essential to impart long-term physical stability to these suspensions, avoiding oil phase separation, in spite of the relatively high values of mean particle volume diameters ($d_{4,3} = 359.1\ \mu\text{m}$ for chitin particles and $d_{4,3} = 176.4\ \mu\text{m}$ for chitosan particles). Thus, for instance, these biopolymers do not produce stable dispersions in paraffinic or naphthenic mineral oils. This fact suggests a partial compatibility between these biopolymers and vegetable oils, yielding a good particles dispersion and uniform microstructure, as can be deduced from the micrograph shown in Fig. 6a for the CC-21 system. However, a very thin layer of separated oil can be detected after 9–10 months of ageing due to a certain degree of particles sedimentation.

This above mentioned evolution of SAOS functions with frequency, typically found in highly entangled polymeric systems (Ferry, 1980), is very similar to that shown by commercial lubricating greases (Madiedo, Franco, Valencia, & Gallegos, 2000; Sánchez, Franco, Valencia, et al., 2011). As extensively investigated (Delgado et al., 2006a; Franco et al., 2005; Martín-Alfonso, Moreno, et al., 2009; Martín-Alfonso, Valencia, Sánchez, Franco, & Gallegos, 2007; Martín-Alfonso, Valencia, et al., 2009; Moreno et al., 2008), typical G' values in lubricating greases of NLGI grade 1–2 range from 10^4 to 10^5 Pa, around one decade higher than G'' values, depending on composition and processing conditions. This range of G' and G'' values can be matched by using chitin concentrations comprised between 19 and 23% (w/w) (see Fig. 4a). The relative elasticity of chitin-based oleogels is also similar to that found in standard greases, as shown in Fig. 4b, where the values of the loss tangent ($\tan\delta = G''/G'$) are plotted versus frequency (Martín-Alfonso, Valencia, et al., 2009; Moreno et al., 2008). As can be observed, oleogel relative elasticity increases with chitin concentration in a wide frequency range. Furthermore, a significant decrease in G' and G'' values was found when castor oil was replaced by a less viscous oil, such as soybean oil. This fact must be also attributed to a decrease in the above mentioned polar interactions between the oil and chitin, as a consequence of replacing the ricinoleic acid,

Table 5
TGA characteristic temperatures for selected oleogels and some standard lithium lubricating greases.

	T_{onset} (°C)	T_{max} (°C)	T_{final} (°C)	Residue (%)
CC-21	351/442	379/459	396/486	5.8
MMC-25	282/369	300/390	311/414	7.1
LMC-39	281/367	300/389	311/409	14.4
A2MMC-35	203/358	240/388	262/414	6.2
A3MMC-35	211/359	234/393	256/428	3.2
Standard paraffinic oil-based grease	188	245	–	3.8
Standard naphthenic oil-based grease	229	295	326	1.3

the main fatty acid in the castor oil, by other fatty acids without hydroxyl groups, in the case of soybean oil.

On the other hand, much higher values of the linear viscoelasticity functions are found for physically stable chitosan-based oleogels (Fig. 5), around one decade higher than those obtained for chitin-based oleogels, as a consequence of the higher degree of deacetylation which allows to form more favourable C═O H–N hydrogen bond interactions (Uragami & Tokura, 2006), resulting in stronger oleogels. As previously remarked, it is also clearly noticed that the values of both SAOS functions for MMC-based oleogels increase with thickener concentration (Fig. 5a). Moreover, a slight decrease in G' and no significant differences in G'' are found when

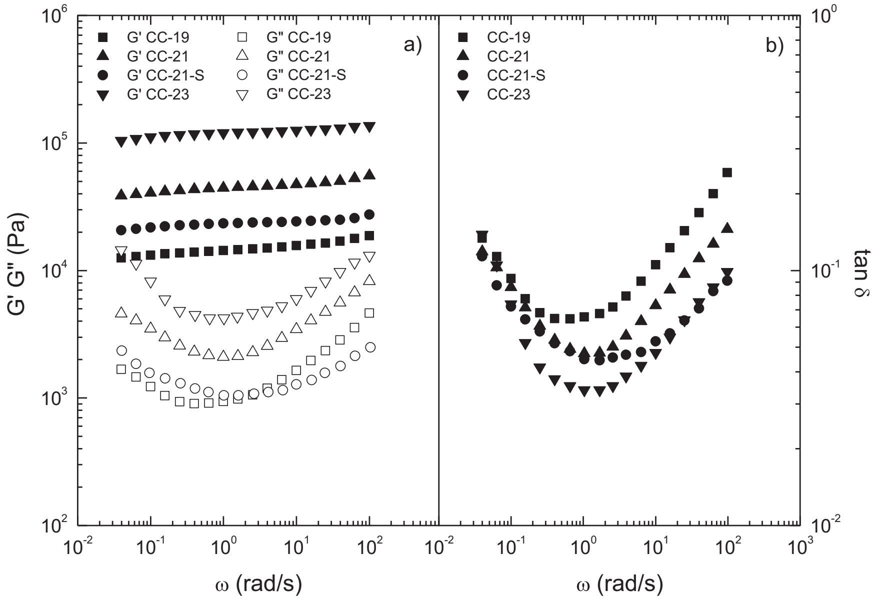

Fig. 4. Evolution of SAOS functions with frequency for chitin-based oleogel formulations, at 25 °C.

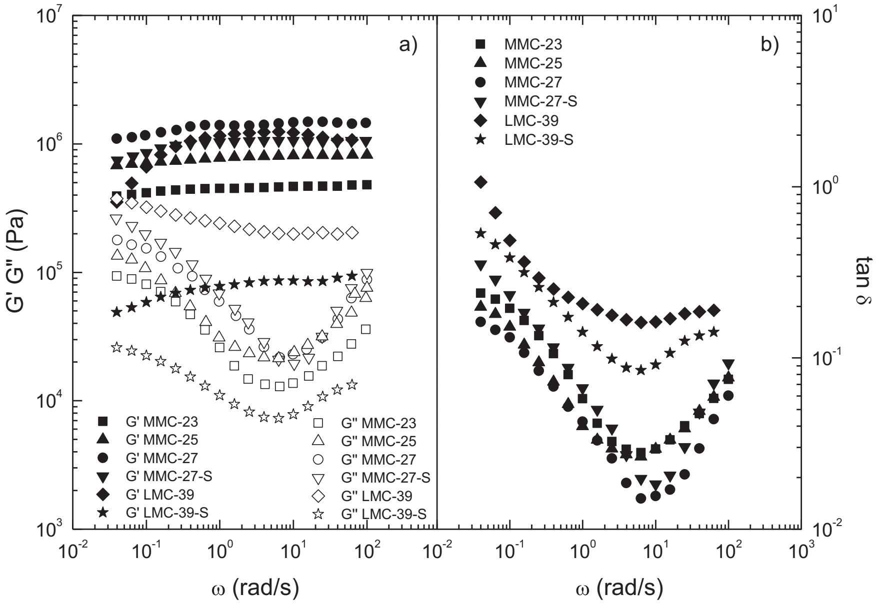

Fig. 5. Evolution of SAOS functions with frequency for chitosan-based oleogel formulations, at 25 °C.

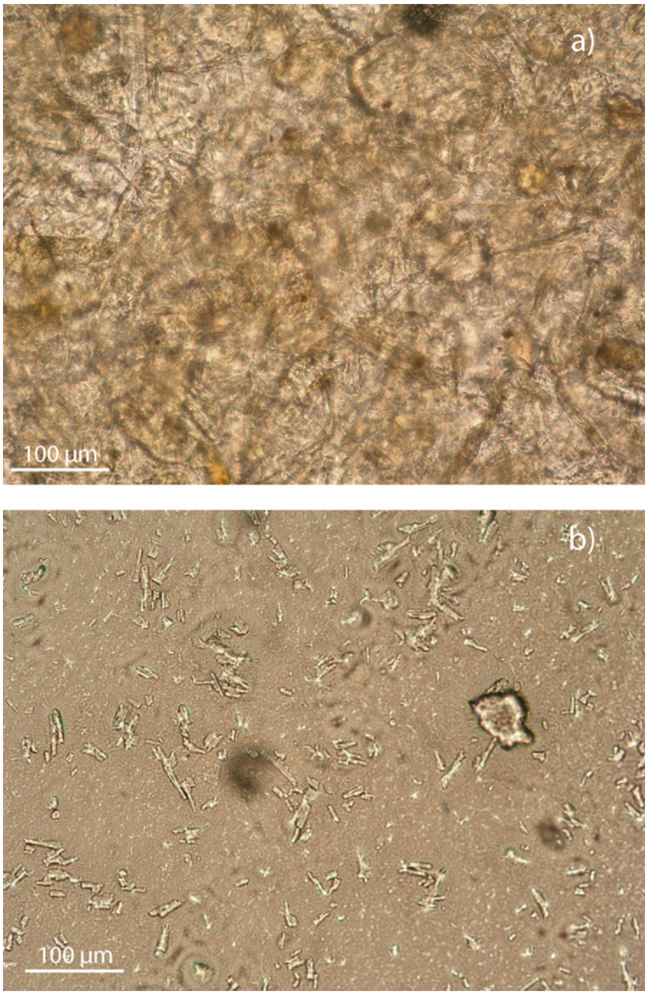

Fig. 6. Optical microscopy observations of microstructures corresponding to (a) a chitin-based oleogel (CC2-1) and (b) an acylated chitosan-based oleogel (A3MMC-35).

castor oil is replaced by soybean oil. The loss tangent is slightly affected by chitosan concentration (slight decrease as thickener concentration increases) or type of oil (slightly higher for castor oil-based oleogels). If a low-molecular weight-chitosan (LMC) is used as thickener, instead of MMC, higher concentrations of biopolymer are required to produce a stable dispersion, avoiding phase separation and also reducing the grainy aspect of the samples, which turn to show a much more homogeneous appearance. At least, 35% (w/w) LMC is necessary to achieve physically stable oleogels. However, at this concentration, a rather different mechanical spectrum with no developed "plateau" region is obtained. This "plateau" region develops as thickener concentration increases. In this sense, a crossover between both linear viscoelastic functions, at low frequencies, followed by the previously mentioned "plateau" region, are noticed for castor oil oleogels containing 39% LMC. Thus, as expected, the gel-like microstructure induced by the low-molecular weight-chitosan presents a lower value of the main relaxation time, as the crossover between the SAOS functions indicates. However, in spite of the different mechanical spectrum, for this thickener concentration, G' values are similar to those obtained for MMC-based oleogels, whilst G'' values are even higher (Fig. 5a). Consequently, the values of the loss tangent are higher and the relative elasticity of LMC-based castor oil oleogel decreases (Fig. 5b). As previously discussed for chitin-based oleogels, the replacement of castor oil by soybean oil significantly reduces the values of the SAOS functions, yielding a rheological behaviour much more similar to that shown by standard lubricating greases. In the case of the oleogels formulated with soybean oil, once again, LMC generates a more relative viscous response than MMC.

An alternative for reducing the values of the SAOS functions is the use of acylated chitosan as thickener. Fig. 7 shows the mechanical spectra of oleogels formulated with castor oil and different acylated chitosan thickeners. As can be observed, both linear viscoelasticity functions decrease by using acylated biopolymers. In addition, a well-developed plateau region is always noticed, excepting for A3LMC-35 oleogel, which shows rather low values of both functions as well as a mechanical spectrum typical of much weaker gel network, being close to both crossover points between G' and G'' at low and high frequencies. In general, SAOS functions decrease as the substitution degree achieved during the acylation reaction increases, either for low or medium molecular weight chitosans. Besides this, it is also apparent that acylated MMC-based oleogels show higher values of the linear viscoelasticity functions, and lower values of $\tan\delta$ (more elastic) than acylated LMC-based products. Thus, together with CC-21 and LMC-39-S systems, the most similar rheological response to that found in traditional commercial lubricating greases (Sánchez, Franco, Valencia, et al., 2011) was achieved by using A2MMC, with a low degree of acylation (see Table 2), as thickener agent. However, the most important advantage of using an acylated chitosan is its increased solubility in oil, as a consequence of a lower polarity, resulting in a much more stable and homogenous oleogel. This can be observed in Fig. 6b for the A3MMC-35 system as compared with the chitin-based dispersion. In fact, the thickening mechanism of acylated chitosan is more related to the formation of real gels in hydrophobic media, similarly to that proposed for ethyl cellulose in organic solvents (Chan, Chow, & Heng, 2006; Heng, Chan, & Chow, 2005; Lizaso, Muñoz, & Santamaría, 1999), including vegetable oils (Aiache, Gauthier, & Aiache, 1992). Nevertheless, acylated chitosan-containing oleogels lose their gel-like behaviour at moderate temperatures, turning into very fluid materials at 50 °C, as illustrated in Fig. 8 for A2MMC-35 oleogel. This experimental evidence can be explained taking into account that part of the acylated chitosan starts to melt at 40 °C, as previously discussed (see Fig. 1). Evidently, this fact implies an important limitation for its use in a lubricating grease formulation at high in-service temperatures.

The influence of temperature on the SAOS functions was also analyzed for other selected samples (CC-21 and MMC-25, data not shown). For these oleogels, SAOS functions are not largely influenced by temperature (between 5 and 130 °C). In this sense, a slight decrease in both G' and G'' is observed up to around 100 °C, followed by an increase at higher temperatures. This slight increase noticed in both SAOS functions at high temperatures (>100 °C) may be related to a certain degree of oil separation (oil bleeding) detected after performing the rheological measurement, which increases the effective concentration of the thickener.

Below this critical temperature, the temperature dependence of the plateau modulus G_N^0, defined elsewhere (Baurngaertel, De Rosa, Machado, Masse, & Winter, 1992), can be described by means of an Arrhenius-type equation, as previously reported (Sánchez et al., 2009):

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

where E_a is a fitting parameter that gives information on the oleogel thermal dependence, with a physical meaning similar to an 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). The activation energy values resulting from this fitting were 3701 and 424 J/mol for these two selected chitin- and chitosan-based formulations, respectively. These values are similar or, in the case of chitosan-based oleogels, even lower than those obtained for standard lithium greases in the low-temperature range (1–2 kJ/mol)

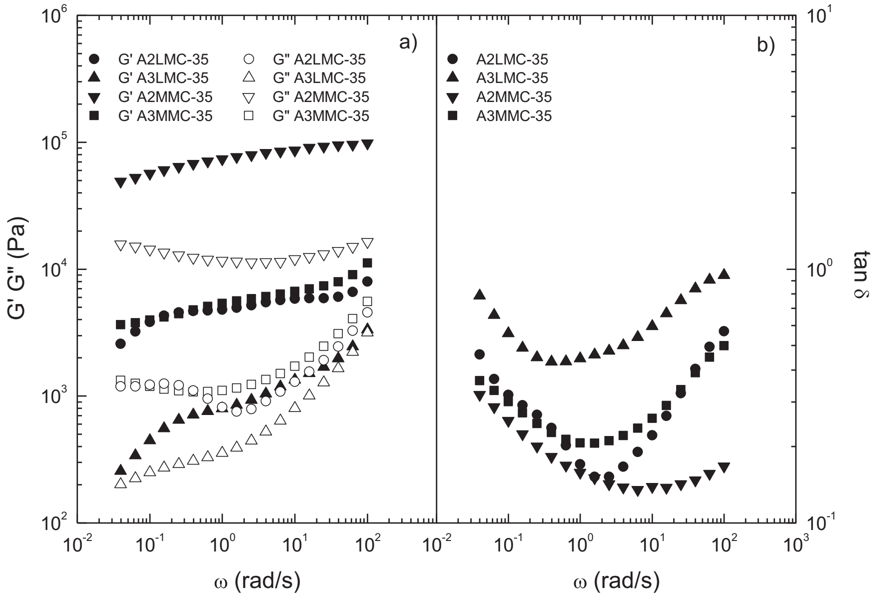

Fig. 7. Evolution of SAOS functions with frequency for acylated chitosan-based oleogel formulations, at 25 °C.

and much lower than those reported in the high-temperature range (18–20 kJ/mol) (Delgado, Valencia, Sánchez, Franco, & Gallegos, 2006b). This thermal dependence is also lower than that shown by other biodegradable lubricating greases based on castor oil and cellulosic derivatives (Sánchez et al., 2009; Sánchez, Franco, Delgado, et al., 2011), although, in those cases, the available range of temperature where oil bleeding is not perceived was much higher.

3.4. Lubrication performance properties

It is well known that the mechanical stability of lubricating greases is traditionally determined from the difference between penetration indexes after and before submitting the grease to a standardized working test. In this study, oleogel mechanical stability was evaluated after the application of a shear rolling test. Greases with good mechanical stability must exhibit penetration increments after working close to zero. Table 6 shows the penetration indexes of the samples studied, as well as standard deviation data, before and after applying the rolling test, as well as the corresponding NLGI grade referred to the non-perturbed sample. The NLGI (*National Lubricating Grease Institute*) grade is a widely accepted parameter to classify lubricating greases as a function of their consistencies obtained as penetration indexes (NLGI, 1994). In general, the NLGI grade increases with thickener concentration and decreases when soybean oil, instead of castor oil, is used in the formulation. As can be observed, chitin-based oleogels show a negative variation of the penetration index. This means that the rolling test induces an increase in consistency, which once again must be attributed to an increase in the effective thickener concentration due to a certain degree of the shear-induced “oil bleeding” observed in these samples after the application of the rolling test. On the contrary, chitosan-based dispersions display a significant

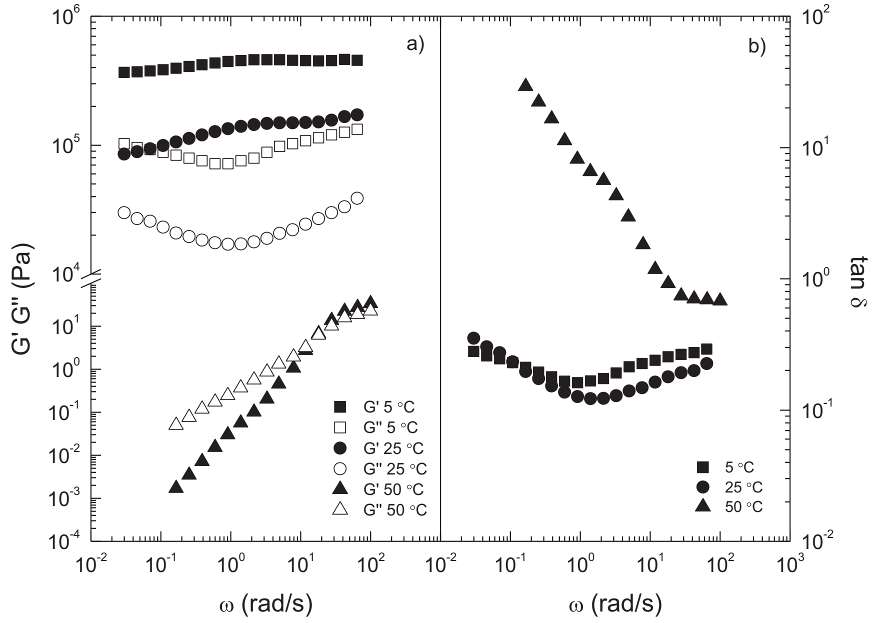

Fig. 8. Evolution of SAOS functions with frequency for A2MMC-based oleogel formulations, at different temperatures.

Table 6
Penetration and mechanical stability values for the oleogels studied, and for some standard lithium lubricating greases.

Sample	Unworked penetration (dmm)	NLGI grade	Worked penetration (dmm)	Penetration variation (dmm)
CC-19	423 ± 3	00	373 ± 2	−50
CC-21	352 ± 3	0–1	320 ± 4	−32
CC-23	302 ± 4	1–2	268 ± 3	−34
MMC-23	358 ± 3	0	407 ± 3	49
MMC-25	295 ± 3	2	325 ± 3	30
MMC-27	248 ± 2	3	310 ± 2	62
MMC-27-S	310 ± 4	1	405 ± 4	95
LMC-39	339 ± 4	1	385 ± 3	46
LMC-39-S	598 ± 5	<000	634 ± 4	36
A2LMC-35	813 ± 4	<000	815 ± 5	2
A3LMC-35	563 ± 5	<000	674 ± 4	111
A2MMC-35	363 ± 4	0	423 ± 4	60
A3MMC-35	537 ± 5	<000	474 ± 3	−63
Standard paraffinic oil-based grease	303 ± 4	1–2	305 ± 4	2
Standard naphthenic oil-based grease	312 ± 4	1	336 ± 4	24

Table 7
Friction coefficient values for selected oleogels and a standard lithium lubricating grease.

Sample	Friction coefficient
CC-21	0.25 ± 0.02
MMC-25	0.16 ± 0.01
A2MMC-35	0.12 ± 0.01
Standard naphthenic oil-based grease	0.14 ± 0.01

positive variation of penetration indexes. Only a few samples with penetration variations around 30–40 dmm can be considered moderately stable and comparable to standard lithium greases. Finally, formulations containing acylated chitosan show, in general, very low consistency and poor mechanical stability.

The potential applicability of these oleogels as biodegradable lubricating greases has been also investigated in a tribological contact. Table 7 shows the friction coefficient values, and corresponding standard deviations, obtained in a ball-disc nanotribometer for selected oleogel samples. With the exception of the formulation containing chitin as thickener, which exhibits a much higher friction coefficient, the remaining oleogel samples studied show a satisfactory response. Thus, the friction coefficient value obtained with the chitosan-based dispersion is only slightly higher than that found for naphthenic oil-based lithium grease, whilst the use of an acylated chitosan as thickener provides a friction coefficient even lower.

4. Conclusions

In this work, the use of chitin, chitosan and some acylated derivatives to obtain gel-like dispersions in vegetable oils, potentially applicable as a biodegradable alternative to lubricating greases, was explored. Different acylated chitosan products with different substitution degree were obtained. Suitable thermal, rheological and tribological properties were found for some of the formulations investigated. The evolution of the linear viscoelasticity functions with frequency, and the orders of magnitude of the linear viscoelasticity functions, for oleogels containing chitin or acylated chitosan, in a characteristic range of thickener concentration, were very similar to those obtained with standard lubricating greases. On the contrary, stable chitosan-based oleogels showed much higher values of both linear viscoelasticity moduli. Higher concentrations of biopolymer were required to produce stable oleogels when using a low-molecular weight-chitosan. In general, SAOS functions increased with biopolymer concentration and decreased when soybean oil was used in the formulation of the oleogel. Acylated chitosans yielded much softer materials, with significantly lower values of both linear viscoelasticity functions, which also decrease with the acylation degree. Linear viscoelasticity functions were not significantly influenced by temperature in the case of chitin and chitosan-based oleogels. On the contrary, formulations containing acylated chitosans lost their gel-like behaviour at moderate temperatures, turning into very fluid materials above 40–50 °C. Thermal decomposition of oleogel samples generally occurs in two main stages. The first one corresponds to the decomposition of the biopolymer, whilst the second one is associated to the thermal degradation of the castor oil. Chitin and chitosan-based oleogels presented higher thermal stabilities than formulations containing acylated chitosans as thickener, and much higher than those found for standard naphthenic or paraffinic oil-based greases. Moreover, most of the oleogel samples studied showed satisfactory tribological responses, with low values of the friction coefficient, excepting the formulation containing chitin as thickener. However, most of the oleogels exhibited poor mechanical stability, especially those prepared with acylated chitosans.

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