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Rheology and thermal degradation of isocyanate-functionalized methyl cellulose-based oleogels

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ABSTRACT

The —NCO-functionalization of methyl cellulose with HMDI and its application to chemically gel the castor oil is explored in this work by analyzing the influence of functionalization degree on the rheological and thermogravimetric behavior of resulting chemical oleogels. With this aim, different methyl cellulose chemical modifications were achieved by limiting the proportion of HMDI and, subsequently, oleogels were obtained by dispersing these polymers in castor oil and promoting the reaction between those biopolymers and the hydroxyl groups located in the ricinoleic fatty acid chain. —NCO-functionalized methyl cellulose-based oleogels were characterized from themogravimetric and rheological points of view. Suitable thermal resistance and rheological characteristics were found in order to propose these oleogels as promising bio-based alternatives to traditional lubricating greases based on non-renewable resources. In general, —NCO-functionalized methyl cellulose thermally decomposed in three main steps whereas resulting oleogels thermal decomposition takes place in one main single stage which comprises the thermal degradation of both the polymer and the castor oil. Temperature range for thermal degradation is broadened when using highly —NCO-functionalized methyl cellulose. A cross-linked viscoelastic gel was obtained with methyl cellulose functionalized in a relatively low degree (around 6% —NCO molar content). The rheological properties of highly functionalized methyl cellulose-based oleogels evolve during several months of aging, but mainly during the first week, due to the progress of the reaction between —NCO functional groups and castor oil —OH groups. SAOS functions analyzed and oleogel relative elasticity increase with the functionalization degree. Oleogel linear viscoelastic response is also extremely dependent on NCO-functionalized methyl cellulose concentration.

1. Introduction

As has been collected in several reviews (Abdallah & Weiss, 2000; George & Weiss, 2006; Gronwald, Snip, & Shinkai, 2002; Kumar & Katare, 2005; Terech & Weiss, 1997; Vintiloiu & Leroux, 2008), an extensive literature on organogels and the finding of low-molecular weight and polymeric appropriated gelators of non-aqueous systems, including triacylglyceride oils (Behera, Patil, Sagiri, Pal, & Ray, 2012; Co & Marangoni, 2012; Laredo, Barbut, & Marangoni, 2011; Sánchez, Franco, Delgado, Valencia, & Gallegos, 2008; Toro-Vazquez, Morales-Rueda, Mallia, & Weiss, 2010), has been published in the past two decades, which reflects the increasing attention and potential applications of these materials. Among these organogelators, some carbohydrates (Cheuk, Stevens, & Wang, 2009; Friggeri, Gronwald, Van Bommel, Shinkai, & Reinhoudt, 2002; Grassi et al., 2011; Gronwald & Shinkai, 2001; Teramoto & Shibata, 2006) and, particularly, cellulose derivatives (Chan, Chow, & Heng, 2006; Heng, Chan, & Crow, 2005; Laredo et al., 2011; Lizaso, Muñoz, & Santamaría, 1999; Rafferty, Jones, & Andrews, 2009; Rivas-Orta, Antonio-Cruz, Rivera-Armenta, Mendoza-Martinez, & Ramirez-Mesa, 2010; Ruiz-Martinez, Muñoz de Benavides, Morales Hernández, & Gallardo Lara, 2003; Zoumpanioti, Merianou, Karandreas, Stamatis, & Xenakis, 2010) have been proposed to gel different organic liquids, in most cases for biotechnological and pharmaceutical applications. For instance, special interest aroused ethyl cellulose-based gels in non-aqueous polar solvents, which have been recently investigated as topical drug delivery systems (Bruno et al., 2011; Bruno, Kasapis, & Heng, 2012a, 2012b).

However, other potential applications of organogels, and particularly oleogels, need further investigation. Nowadays, one of the main problems of different industrial sectors concerns the impact

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that process technologies and products cause in the environment and, therefore, there is a general tendency to promote the replacement of non-renewable raw materials by renewable resources. Such environmental problems may result dramatic in the case of the lubricant industry (Bartz, 1998; Boyde, 2002; Wilson, 1998). Although vegetable oils are being increasingly used as lubricant base oils instead of mineral and synthetic oils, the substitution of traditional thickener agents, such as lithium, aluminum, sodium or calcium soaps, in lubricating greases by others derived from renewable resources, like some biopolymers, is a complicated task due to the technical efficiency of metallic soaps to impart the desired rheological, thermal and tribological properties to the bulk system. The use of cellulose and chitosan derivatives-based physical oleogels and gel-like dispersions as biodegradable or environmentally friendly lubricating grease formulations were extensively explored in previous studies (Nuñez et al., 2011; Nuñez, Martín-Alfonso, Eugenio, et al., 2012; Nuñez, Martín-Alfonso, Valencia, Sánchez, & Franco, 2012; Sánchez, Franco, Delgado, Valencia, & Gallegos, 2009, 2011a, 2011b; Sánchez, Stringari, Franco, Valencia, & Gallegos, 2011). Methylated and ethylated cellulose derivatives or the combination of both of them, provided gel-like dispersions with promising rheological and thermal properties to be used as lubricating greases. However, some weaknesses were observed regarding their physical and mechanical stabilities under quiescent and working conditions, respectively. As it was previously reported (Sánchez, Franco, Delgado, et al., 2011a), the role of ethyl cellulose, by gelling vegetable oils and thus modifying their rheological characteristics, is essential to impart long-term physical stability to these gel-like dispersions. However, in these cases, suitable mechanical and physical stabilities were associated to values of the linear viscoelastic functions much higher than those required for standard greases. In this sense, it is necessary to investigate the performance of other alternatives which could fit the whole set of relevant properties for a lubricating grease. More recently (Gallego, Arteaga, Valencia, & Franco, 2013), the functionalization of methyl cellulose with reactive isocyanate groups and its ability to thicken castor oil by reacting with the hydroxyl groups of the ricinoleic fatty chain was investigated. Resulting chemical oleogels may serve to different applications depending on the functionalization degree. A highly functionalized polymer, obtained by using an excess of the diisocyanate compound, yields a sticky and highly cross-linked material based on polyurethane segments with potential applications as bio-based adhesives or coatings (Deka & Karak, 2009; Kong, Liu, & Curtis, 2011; Mishra & Sinha, 2010). On the contrary, oleogels obtained with methyl cellulose functionalized in lower degree presented suitable rheological properties and thermal resistance to be used as lubricating grease, as well as long-term physical stability due to the progress of the chemical reaction between the —NCO-functionalized biopolymer and the hydroxyl groups located in the ricinoleic fatty acid chain of castor oil. As a continuation of this research, a more systematic study on the —NCO-functionalization degree of methyl cellulose is carried out and its influence on the rheological and thermogravimetric response of resulting chemical oleogels is analyzed in this work.

2. Experimental

2.1. Materials

Castor oil (211 cSt at 40 °C, Guinama, Spain) was selected as biodegradable lubricating base oil for oleogel preparations. Methyl cellulose (M_n 40,000 g/mol; 58% methoxy groups) was modified with 1,6-hexamethylene diisocyanate (HMDI, purum grade, ≥98.0%), both from Sigma–Aldrich. All other common reagents and solvents employed were purchased from Sigma–Aldrich.

2.2. General methods

Functionalization reactions were performed in flasks that were flame-dried under a positive flow of argon to eliminate surface moisture after assembly and conducted under argon. HMDI was stored at 4 °C and handled under inert (argon) atmosphere. Solvents were purified according to standard literature techniques and stored under argon. Toluene was freshly distilled immediately prior to use from sodium/benzophenone and strictly deoxygenated for 30 min under argon. Reagents were purchased at the higher commercial quality and used without further purification, unless otherwise stated. Characterization tests were performed at least in duplicate.

2.3. Functionalization reaction of methyl cellulose with HMDI

The reaction of methyl cellulose functionalization was carried out following the protocol previously described (Gallego et al., 2013). Methyl cellulose was added to a bottom round flask with toluene while stirring at room temperature becoming a suspension. Then, triethylamine (Et_3N) and HMDI were also added to the system, the last one dropwisely. The solution was vigorously stirred at room temperature during 24 h. The synthesis was carried out under inert atmosphere of argon. Afterwards, the mixture was vacuum filtered resulting in a white powder. The product was not stored but immediately used to prepare the oleogels. With the aim of controlling the ratio of functionalized —OH groups in the cellulose derivative synthesized, the amounts of HMDI, Et_3N and toluene were modified. The different ratios of HMDI, Et_3N and toluene with respect to starting material used in the reaction are listed in Table 1. Molar calculation was made on the basis of methyl cellulose monomer. In this sense, 58% of the three —OR groups are in form of —OMe and the rest in the form of —OH, so there are 1.25 mol of free —OH in each monomer. On the other hand, it was used minimal amount of toluene to achieve a proper solution of the reagents, thus preventing the influence of the concentration on the results obtained. The different degrees of functionalization achieved for modified methyl cellulose polymers, determined by ^{1}H NMR spectroscopy, are listed in Table 2.

2.4. Preparation of oleogels

Oleogel samples were prepared in an open vessel, using a controlled-rotational speed mixing device (70 rpm) RW 20

Table 1
Proportion of methyl cellulose, hexamethylene diisocyanate (HMDI), triethylamine (Et_3N) and toluene used in the functionalization reactions.

Polymer	Methyl cellulose (equiv.)[a]	HMDI (equiv.)[a]	Et_3N (equiv.)[a]	Toluene (ml)
MC–NCO-1	1.0	6.8	21	300
MC–NCO-2	1.0	4.8	9.5	200
MC-NCO-3	1.0	2.4	4.8	100
MC–NCO-4	1.0	1.2	2.4	100
MC–NCO-5	1.0	0.7	1.4	100
MC–NCO-6	1.0	0.3	0.6	100

[a] Equivalents refer to the proportion between moles of free —OH groups present in each sugar monomer of starting methyl cellulose, and moles of each of the reagents.

Table 2
Substitution degree over —OH groups of modified methyl cellulose polymers.

	—OR % molar[a]		
	R=Me	R=H	R = CNH-$(CH_2)_6$-NCO
MC–NCO-1	58	1	41
MC–NCO-2	58	3	39
MC–NCO-3	58	6	36
MC–NCO-4	58	16	26
MC–NCO-5	58	36	6
MC–NCO-6	58	41	1

[a] Data obtained from ^{1}H NMR spectra.

(Ika), equipped with an anchor impeller to disperse the different biopolymers in the oil. Functionalized biopolymers were slowly added to the oil at concentrations of 25%, 30% and 35% (w/w) under agitation (70 rpm). Agitation was maintained for 24 h at room temperature. Finally, the resulting dispersion was homogenized with an Ultra-Turrax T50 (Ika) rotor-stator turbine, at 8800 rpm during 1 min. Batches of 60 g were prepared for each formulation investigated. Different oleogels are identified below with the biopolymer code (see Table 2) followed by its concentration.

2.5. Thermogravimetric analysis (TGA)

Measurements of mass loss versus temperature were carried out by using a thermogravimetric analyzer, model Q-50 (TA Instrument Waters, USA) under N_2 purge. 5–10 mg of sample were placed on a platinum pan and heated from 30 °C to 600 °C, at 10 °C/min. TGA tests were performed immediately after modification with HMDI, for methyl cellulose-derived polymers, and 1 month after preparation, in the case of oleogels.

2.6. Nuclear magnetic resonance of protons (^{1}H NMR)

NMR spectra of functionalized methyl cellulose samples were recorded with a Varian Direct-Drive 500 (^{1}H 500 MHz) spectrometer using DMSO-d_6 as solvent.

2.7. Fourier transform infrared spectroscopy (FTIR)

FTIR spectra were obtained with a Digilab FTS3500ARX (Varian) apparatus. Biopolymer samples were prepared as KBr pellets, whereas a small drop of oleogels was placed between two KBr disks (32 mm × 3 mm). Then, in both cases, the set was 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.

2.8. Rheological characterization

Rheological characterization of oleogels was carried out with a Gemini controlled-stress rheometer (Bohlin, UK). Small-amplitude oscillatory shear (SAOS) tests were performed inside the linear viscoelastic region, using a plate-plate geometry (25 mm, and 1 mm gap), in a frequency range of 10^{-2}–10^2 rad/s, at 25 °C. Previously, stress sweep tests, at 1 rad/s, were carried out in order to determine the linear viscoelastic range. Measurements were done 1 day, 1 week, 1 month and 4 months after oleogel preparation.

Table 3
^{1}H NMR representative signals (chemical shift and relative peak areas) for a selected polymer (MC–NCO-4).

MC–NCO-4		
Type of proton	δ (ppm)	Relative area
C—H (aromatic of toluene)	7.1 (s, 2 H), 7.2 (s, 1 H)	1.85
N—H	5.7 (s, 1 H)	0.97
CH_2—NCO and O—CH_3	3.3 (s, 5 H)	5.27
NH—CH_2	2.9 (s, 2 H)	1.48
CH_2—OCH_3	2.3 (s, 2 H)	1.79
4× CH_2 (intermediate aliphatic chain of HMDI)	1.2–1.5 (m, 8 H)	7.95

3. Results and discussion

3.1. Chemical characterization of isocyanate-functionalized methyl cellulose samples and derived oleogels

Following the methodology previously described (Gallego et al., 2013), the different substitution degrees of modified methyl cellulose polymers were calculated based on their ^{1}H NMR spectra. It was found a significant difference in the proportion of functionalized —OH groups, being proportional to the amount of HMDI employed as functionalizing reagent (Table 1). In NMR spectrometry, the ratios of —OMe, —NCO and —OH groups were calculated by comparing the integrals of two regions of the ^{1}H NMR spectra (see Table 3): the first one includes the overlapped peaks assigned to —CH_3 protons of the —OMe group and those corresponding to protons of —CH_2— group adjacent to the free —NCO group of HMDI once reacted (3.3 ppm); the second region is that corresponding to the peak due to —CH_2— protons attached to —N—H group at the end of reacted HMDI chain (2.9 ppm). The two overlapped peaks in the first region were separated using the signal corresponding to —N—H proton, which must be proportional to the —NCO signal in a 1:1 ratio, as reference (5.7 ppm). Based on the value of the integrals areas of —OMe and —CH_2— groups next to —N—H group, a ratio between them was established. By relating this ratio to the fact that the commercial methyl cellulose used had a degree of substitution of 58%, the average occupation of each position in the monomer of methyl cellulose was calculated (Table 2).

Chemical modification of methyl cellulose after the functionalization with different proportions of HMDI and further reaction with the hydroxyl groups of castor oil were also evaluated by FTIR. Fig. 1 shows the FTIR spectra of starting methyl cellulose, one selected functionalized sample (MC–NCO-4) and the corresponding oleogel prepared with this polymer and castor oil (MC–NCO-4-30), respectively. Infrared spectra of functionalized biopolymers were in concordance with the proposed chemical structure (Gallego et al., 2013). Table 4 lists the most important peaks detected in these chemically modified polymers. A significant reduction in the intensity of the band at 3468 cm^{-1}, attributable to the —OH moieties in methyl cellulose, was observed once reacted with isocyanate groups of HMDI leading to urethane linkages. The higher HMDI content, the higher reduction in this band is. Secondly, the urethane

Table 4
IR representative signals for a selected NCO-functionalized methyl cellulose sample (MC–NCO-4).

Functional group	Wavenumber (cm^{-1})
OH + NH	3468
C—H aliph.	2934
N=C=O	2271
C=O	1723
N—H	1561
C—N or C—OH	1259
C—O or C—O—C	1117

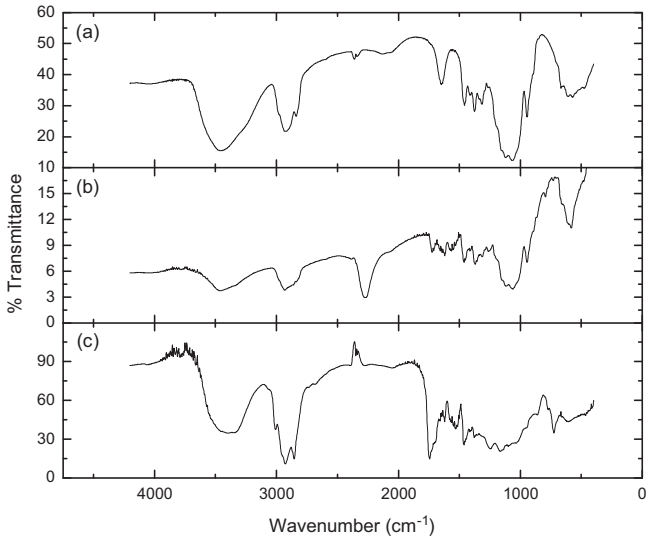

Fig. 1. FTIR spectra for (a) methyl cellulose, (b) polymer MC–NCO-4 and (c) oleogel MC–NCO-4-30.

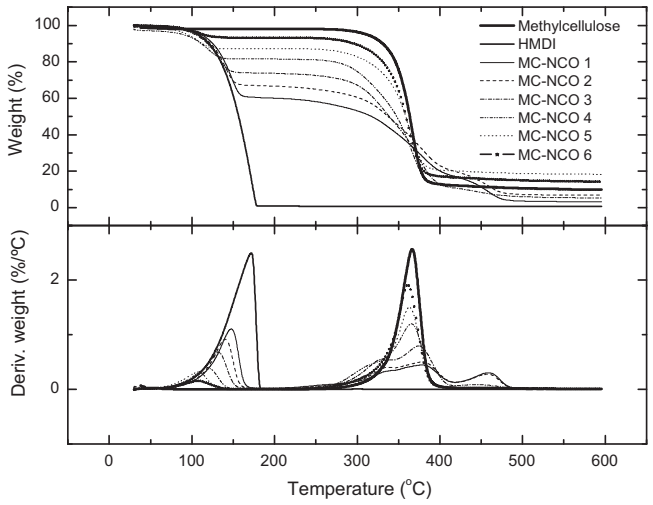

Fig. 2. Thermal degradation curves, under inert atmosphere, for the NCO-functionalized methyl cellulose polymers studied and starting materials used in the functionalization.

bands were apparent at 3468 (—N—H), 1723 (C═O urethane), and 1561 cm^{-1} (—N—H urethane) in all modified biopolymers. Moreover, the intense peak at 2271 cm^{-1} confirmed the presence of free isocyanate groups, as intended (Fig. 1b). The reaction between —NCO and —OH groups of functionalized methyl cellulose and castor oil, respectively, was monitored by analyzing the FTIR spectra of oleogels. Fig. 1c shows the FTIR spectrum for a selected oleogel sample (MC–NCO-4-30). As can be seen, the absorption band assigned to free —NCO at 2271 cm^{-1} is negligible in the IR spectrum of resulting oleogel (Fig. 1c), which corroborates the occurrence of the reaction promoted.

3.2. *Thermogravimetric characterization of isocyanate-functionalized methyl cellulose samples and derived oleogels*

Thermal degradation of methyl cellulose (MC) and derived —NCO-functionalized compounds (MC–NCO) was studied by means of thermogravimetric analysis (TGA). Fig. 2 shows TGA curves, in the form of weight loss versus temperature and its derivative function, as a function of the functionalization degree. The temperature for the onset of thermal decomposition (T_{onset}), the temperature at which decomposition rate is maximum (T_{max}), loss weight at the end of each decomposition step and the percentage of non-degraded residue have been estimated from the thermograms of the samples studied, as indicated elsewhere (Sánchez, Franco, Delgado, Valencia, & Gallegos, 2009), and collected in Table 5. For methyl cellulose, thermal degradation under nitrogen atmosphere occurred in one single stage between 347 °C and 378 °C with a significant weight loss (89%). However, for isocyanate-functionalized methyl cellulose, the inclusion of HMDI segments into the polymer structure reduces their thermal stabilities (Fig. 2 and Table 5). Thermal decomposition of these polymers takes place in several stages depending on HMDI content. Generally, this decomposition occurs in three different stages for MC–NCO samples. The first one at around 82–123 °C, with temperatures for the maximum decomposition rate, T_{max}, at around 107–147 °C, corresponds to the loss of —NCO segments, which is corroborated with the HMDI thermal degradation occurring in one single stage at 137 °C (Fig. 2). As can be observed in the mass loss vs. temperature derivative curve, the T_{onset} for this degradation stage increases with —NCO content. The second thermal degradation process, at around 310–336 °C, with temperatures for the maximum decomposition rate at 361–378 °C, is mainly due to methyl cellulose chain thermal degradation. Finally, the third degradation stage at 443–458 °C, is only detectable in the most functionalized samples (MC–NCO-(1–3)), and can be assigned to excessively cross-linked methyl cellulose fractions originating more rigid polyurethanes (Mythili, Malar Retna, & Gopalakrishnan, 2004). As can be deduced from Table 5, the modified methyl cellulose sample with higher —NCO content (MC–NCO-1) exhibited higher weight loss in the first stage, at around 39%, which decreases with isocyanate content. On the contrary, the weight loss assigned to the second thermal degradation process becomes more important as functionalization degree decreases. Besides this, the higher amounts of residues were obtained for the lowest functionalized methyl cellulose samples (MC–NCO-(5–6)).

As can be observed in Fig. 3, thermal decomposition of methyl cellulose derivatives-based oleogels takes place in one single stage at around 328–347 °C, with T_{max} values at around 374–380 °C. Therefore, thermal resistance is higher than that generally exhibited by mineral oil-based traditional greases (Martín-Alfonso, Valencia, Sánchez, Franco, & Gallegos, 2009). This decomposition

Table 5
TGA characteristic parameters for NCO-functionalized methyl cellulose samples studied.

Sample	T_{onset} (°C)	T_{max} (°C)	T_{final} (°C)	ΔW (%)	Residue (%)
Methyl cellulose	347	367	378	89	9.8
HMDI	137	172	178	99	0.6
MC–NCO-1	123/310/440	147/378/458	157/398/476	39/43/14	3.1
MC–NCO-2	117/311/440	141/378/458	151/398/476	32/48/13	6.7
MC–NCO-3	107/315/431	132/375/443	144/393/480	26/63/5	5.2
MC–NCO-4	95/323	119/365	133/383	17/73	9.2
MC–NCO-5	84/334	107/363	121/380	14/71	15.9
MC–NCO-6	82/336	107/361	125/377	7/79	14.2

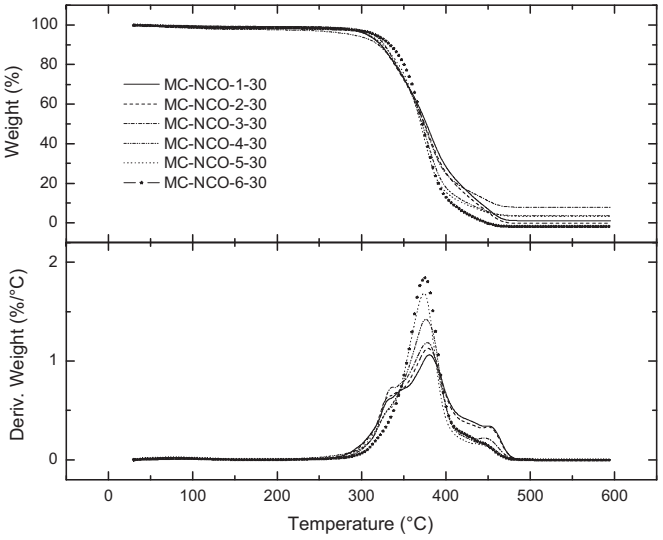

Fig. 3. Thermal degradation curves, under inert atmosphere, for the NCO-functionalized methyl cellulose-based oleogels studied.

Table 6
TGA characteristic parameters for NCO-functionalized methyl cellulose-based oleogels.

Sample	T_{onset} (°C)	T_{max} (°C)	T_{final} (°C)	Residue (%)
MC–NCO-1-30	328	333/380/451	467	1.02
MC–NCO-2-30	330	334/379/450	467	0.29
MC–NCO-3-30	332	336/378/445	465	7.90
MC–NCO-4-30	339	376	463	3.69
MC–NCO-5-30	340	374	462	3.10
MC–NCO-6-30	347	375	460	0.20

temperature range comprises the thermal degradation of both the —NCO-functionalized methyl cellulose previously discussed and the castor oil (Nuñez et al., 2011), the main oleogel component. As can be expected, attending to the previous discussion, this temperature range is broaden when using highly functionalized methyl cellulose (Table 6), since the polymer starts to degrade earlier and also shows a final degradation step above 430 °C that, in this case, is overlapped with the main degradation peak. In those cases where a clear shoulder was observed in the weight loss versus temperature derivative curve, T_{max} values were also indicated in Table 6. Finally, the disappearance of the first polymer degradation peak in the resulting oleogel confirms the chemical reaction promoted between the isocyanate-functionalized methyl cellulose and the castor oil.

3.3. Rheology of isocyanate-functionalized methyl cellulose-based oleogels

Fig. 4 shows the evolution of the linear viscoelasticity functions with frequency, as a function of aging time, for a selected oleogel prepared by dispersing isocyanate-functionalized methyl cellulose in castor oil at 30% (w/w) concentration. In general, the frequency dependence is qualitatively similar to that found in other cellulose derivatives-based gel-like dispersions physically stabilized (Nuñez et al., 2011, 2012a; Sánchez et al., 2009; Sánchez, Franco, Delgado, et al., 2011a). As can be observed, G' is always higher than G'' in the whole frequency range studied, and the plateau region of the mechanical spectrum followed by the beginning of the transition region was always noticed. This mechanical spectrum corresponds with the definition given by Almdal, Dyre, Hvidt, and Kramer (1993) for solid-like gels. Moreover, the values of the SAOS functions are very similar to those exhibited by traditional lubricating greases (Delgado, Valencia, Sánchez, Franco, & Gallegos, 2006; Martín-Alfonso et al., 2009; Sánchez, Franco, Valencia, et al., 2011) and around one decade lower than those found in non-functionalized methyl cellulose gel-like dispersions previously studied (Sánchez et al., 2009). In fact, moderately physically stable methyl cellulose dispersions in castor oil can be obtained only above the percolation threshold, at around 35% (w/w) concentration (Sánchez et al., 2009). As previously reported (Gallego et al., 2013), below this threshold methyl cellulose dispersions became unstable, identically to those prepared with functionalized methyl cellulose and other vegetable oil without —OH groups in the fatty acids. This experimental evidence indicates that the chemical interaction between —NCO functional groups and castor oil —OH groups, thus inducing a real gelation during the methyl cellulose dispersion

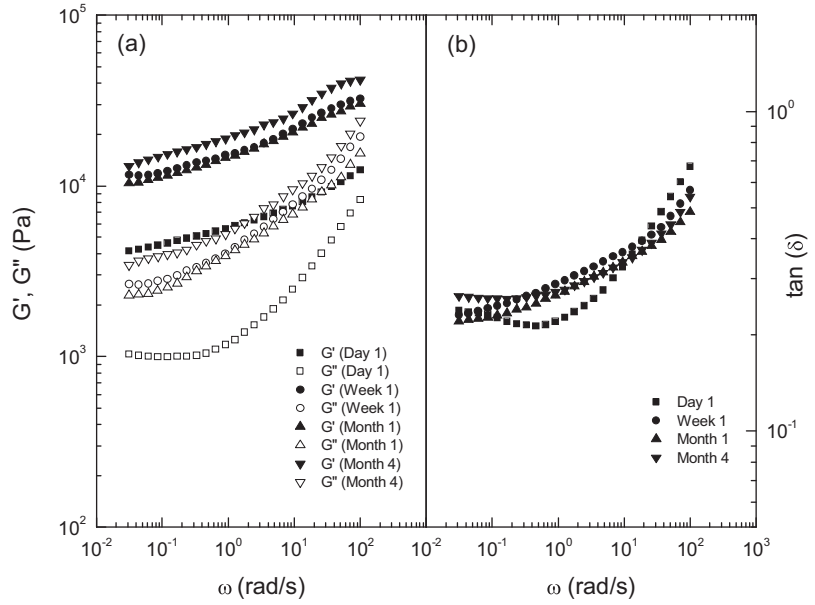

Fig. 4. Frequency dependence of (a) the storage, G', and loss, G'', moduli and (b) the loss tangent, for a selected NCO-functionalized methyl cellulose oleogel (MC–NCO-4-30) as a function of the aging time (G': full symbols, G'': open symbols).

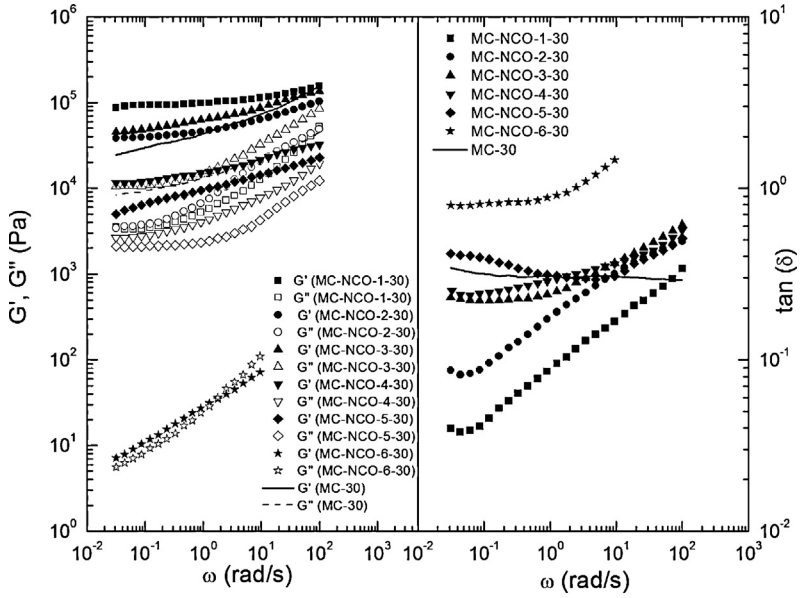

Fig. 5. Frequency dependence of (a) the storage, G', and loss, G'', moduli and (b) the loss tangent, for NCO-functionalized methyl cellulose oleogels, as a function of functionalization degree, 1 week after their preparation (G': full symbols, G'': open symbols).

process, is responsible of the physical stability of these oleogels. Therefore, the methyl cellulose NCO-functionalization procedure allows to obtain stable oleogels with a lower concentration, thus reducing the values of the viscoelastic functions to the level of those exhibited by traditional lubricating greases. As can be observed in Fig. 4, the values of SAOS functions significantly increase during the first seven days of aging and then slightly increase or remain almost constant after several months of aging. These results can be explained on the basis of the slow reactivity of residual —NCO functional groups in a high viscous medium (Moreno et al., 2008). However, interestingly, the loss tangent is almost unaffected (Fig. 4b), which means that the relative elasticity of these systems is not time dependent.

Obviously, —NCO content in the functionalized biopolymer, able to originate cross-linking not only with the oil medium but also among polymeric chains, influences the rheological response. Fig. 5 shows SAOS response of oleogels studied, 1 week after their preparation, as a function of the functionalization degree. According to Lu, Liu, and Tong (2006), the gel strength of chemically induced gels is mainly dependent on the cross-link density. As can be observed, the lowest biopolymer functionalization degree (1% molar substitution) produces almost a critical gel once dispersed in castor oil. However, a cross-linked gel, with the typical viscoelastic response previously described, was obtained with only 6% of —NCO molar content. G' and G'' values further increases with the functionalization degree, whereas the loss tangent significantly decreases, at least at low frequencies. At intermediate functionalization degrees, a well-developed plateau region can be observed, yielding a minimum in the evolution of the loss tangent with frequency, which tends to very similar values at higher frequencies. This minimum is shifted to low frequencies when using highly functionalized methyl cellulose, i.e. 36–41% free molar —NCO content, resulting predominant power-law evolutions of the SAOS functions in a wide frequency range. Attending to these results, a very low methyl cellulose functionalization degree (1–6% —NCO molar content) largely modifies the rheological response of methyl cellulose dispersions in castor oil, significantly lowering the values of the linear viscoelastic functions. For the sake of comparison, the SAOS functions for the 30% (w/w) non-functionalized methyl cellulose dispersion in castor oil (not physically stable at this concentration) was included in Fig. 5. Nevertheless, a high degree of functionalization increases the values of the SAOS functions above those shown by the non-functionalized methyl cellulose dispersion, as a consequence of an extensive cross-linking. The significant reduction in the values of the loss tangent found in oleogels prepared with the highly functionalized methyl celluloses may also be attributed to a certain degree of cross-linking among polymeric chains in the gel network.

As previously discussed, linkage occurrence between functionalized methyl cellulose and castor oil is dependent on the aging time. This is clearly illustrated in Fig. 6a where the G' values, at 1 rad/s, are plotted versus the biopolymer —NCO content for oleogels aged 1 day, 1 week and 4 months, respectively. During the first days after oleogel preparation, a tendency to find maximum SAOS functions were obtained for methyl cellulose having relatively low free —NCO molar content (around 6%), whereas higher functionalization generally results in a slightly lower gel strength. However, the rheological properties of these highly functionalized methyl cellulose-based oleogels evolve during several months of aging, more dramatically during the first week. In this sense, a monotonic tendency to increase the rheological functions with the functionalization degree was found in the first week of aging and, as expected, the highest rheological modification was achieved for the highest values of free —NCO content. As can be observed, increments in G_1' of more than one decade were obtained for oleogels based on highly functionalized methyl cellulose. After 1 week of aging, the rheological modification is significantly dampened. In addition, it is worth pointing out that aging does not exert a significant influence on oleogel rheology below a certain threshold of —NCO content (below 6% molar substitution). Finally, as previously discussed, the loss tangent is not significantly influenced by aging time, mainly decreasing with the free —NCO content (Fig. 6b) when using methyl celluloses with the lowest and highest functionalization degrees.

Traditionally, lubricating greases are classified according to their consistencies, measured through standard penetration tests, once converted to NLGI grades (between 000 and 6) (NLGI, 2006). Most commonly used greases are those with NLGI grade 2, although softer grades, especially 0 and 1, are sometimes used for improved

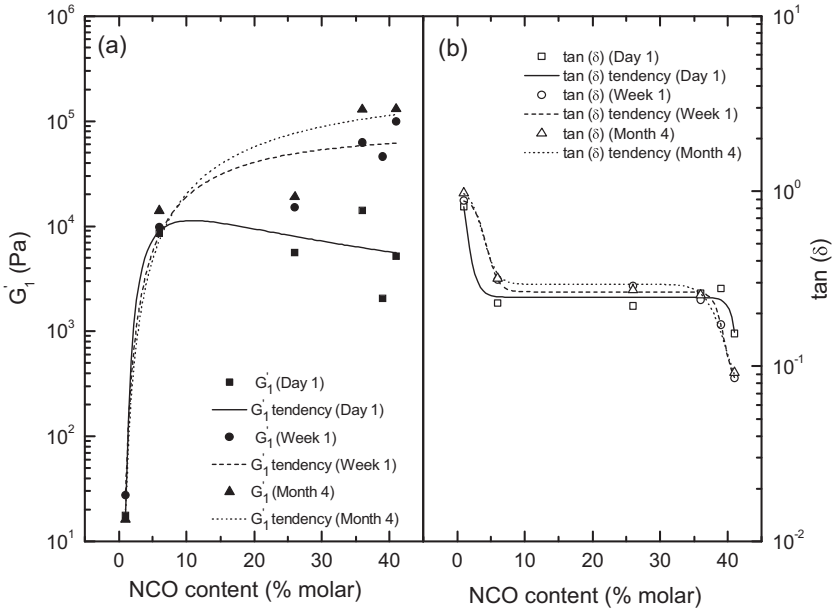

Fig. 6. Polymer molar NCO content dependence of (a) the storage modulus, G'_1, and (b) the loss tangent, at 1 rad/s, for NCO-functionalized methyl cellulose-based oleogels, as a function of aging (G': full symbols, G'': open symbols).

pumpability or low-temperature applications, while higher consistency indexes are used for certain high-speed bearing applications. As extensively investigated (Delgado et al., 2006; Franco, Delgado, Valencia, Sánchez, & Gallegos, 2005; Martín-Alfonso, Valencia, Sánchez, Franco, & Gallegos, 2007, 2009), G' values for NLGI2 lubricating greases based on metallic soaps as thickener agents typically range from 10^4 to 10^5 Pa, around one decade higher than G''. This range of values for both SAOS functions were achieved in most of the functionalized methyl cellulose-based oleogels presented in Fig. 5, which makes them suitable to be proposed as alternative bio-lubricating greases formulations obtained from renewable resources. As usually performed in the grease industry, desired consistency and/or rheological properties can be mainly adjusted by modifying thickener concentration. Fig. 7a shows the mechanical spectra for oleogels containing different NCO-functionalized methyl cellulose concentration. As can be observed, almost two decades of both SAOS functions can be covered by modifying the thickener concentration between 25% and 35% (w/w). Besides this, the evolution of SAOS functions with frequency slightly depends on methyl cellulose concentration. Thus, lower NCO-functionalized methyl cellulose contents favour the achievement of the transition region at high frequencies, with a crossover between both linear viscoelastic functions for the oleogel containing 25% (w/w) of modified methyl cellulose, whereas a well-developed plateau region in all the frequency range studied was obtained by increasing thickener concentration up to 35% (w/w). Moreover, the relative elasticity also increases with NCO-functionalized methyl cellulose concentration as shown in Fig. 7b, where the displacement of the plateau region to higher frequencies is also clearly depicted.

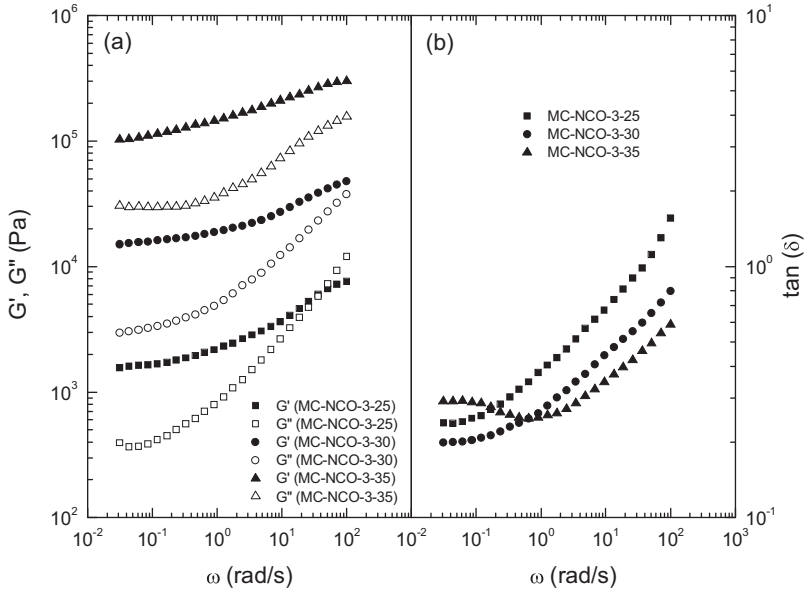

Fig. 7. Frequency dependence of (a) the storage, G', and loss, G'', moduli, and (b) the loss tangent, for NCO-functionalized methyl cellulose-based oleogels, as a function of polymer concentration, 1 week after their preparation (G': full symbols, G'': open symbols).

4. Conclusions

Novel reactive methyl cellulose-derived polymers were synthetized by functionalization with HMDI in several degrees. Chemical oleogels were prepared by dispersing these polymers in castor oil and promoting the reaction between the reactive —NCO group and the hydroxyl group located in the ricinoleic fatty acid chain. Suitable thermal resistance and rheological characteristics were found for these oleogels to be proposed as promising bio-based alternatives to traditional lubricating grease formulations.

Oleogels thermal decomposition takes place in one single stage which comprises the thermal degradation of both the —NCO-functionalized methyl cellulose and the castor oil. Temperature range for thermal degradation is broadened when using highly —NCO-functionalized methyl cellulose.

A cross-linked viscoelastic gel with a well-developed plateau region in the evolution of SAOS functions with frequency was obtained with methyl cellulose functionalized in a relatively low degree (around 6% —NCO molar content). The rheological properties of highly functionalized methyl cellulose-based oleogels evolve during several months of aging, but mainly during the first week, due to the progress of the reaction between —NCO functional groups and castor oil —OH groups. After 1 week, the values of the SAOS functions analyzed and oleogel relative elasticity increase with the functionalization degree. Oleogel linear viscoelastic response is also extremely dependent on NCO-functionalized methyl cellulose concentration.

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