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Influence of molecular weight and free NCO content on the rheological properties of lithium lubricating greases modified with NCO-terminated prepolymers

G. Moreno [a], C. Valencia [a], J.M. Franco [a,*], C. Gallegos [a], A. Diogo [b], J.C.M. Bordado [b]

[a] *Departamento de Ingeniería Química, Facultad de Ciencias Experimentales, Universidad de Huelva, Campus de "El Carmen", 21071 Huelva, Spain*
[b] *Instituto Superior Tecnico, Universidade Técnica de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal*

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ABSTRACT

In this work, the use of reactive diisocyanate-terminated polymeric materials as rheology modifiers of lubricating greases has been studied. Particularly, the influences that free NCO content, molecular weight and functionality of the reactive prepolymers exert on the rheological response and microstructure of lubricating greases were analyzed. With this aim, NCO-terminated prepolymers were prepared from several di and trifunctional polyols and polymeric MDI. Afterwards, the reaction between terminal isocyanate groups and the hydroxy group located in the hydrocarbon chain of the 12-hydroxystearate lithium soap, used as thickener, was promoted during processing of lubricating greases. Polymeric materials used as additives and final lubricating greases were characterized by FTIR, DSC and GPC techniques. The effectiveness of these reactive additives was tested by performing small-amplitude oscillatory shear (SAOS), as well as standardized mechanical stability tests, on final greases. The rheological response was related to the microstructure of these greases, characterized by means of atomic force microscopy (AFM). From the experimental results obtained, it may be concluded that the effectiveness of these polymeric additives to modify the rheology of greases is due to the progress of the reaction between terminal isocyanate groups and the hydroxy group of lithium soap. However, a large dependence on both free NCO content and prepolymer molecular weight was found. Experimental results confirm that a balance between prepolymer molecular weight and NCO content is necessary to reach an optimal rheological modification of lithium greases. Moreover, this balance is a function of grease ageing, due to the progress of the reaction promoted.

1. Introduction

Lubricating greases are highly structured suspensions consisting of a thickener, usually a metal soap, dispersed in mineral or synthetic oil. The most common thickening agent used is lithium 12-hydroxystearate soap. In addition, lubricating greases usually contain same performance additives [1,2]. Thus, the use of polymeric materials is a common practice to modify the rheological properties of greases by reinforcing the role of the thickening agent [3,4]. A new generation of polymeric additives consisting of polyols containing grafted reactive functional groups has been recently investigated. These reactive groups are able to react with alkaline components of the soap [5], enhancing the three-dimensional structural network achieved during the manufacturing process. In addition, polymers functionalized with terminal isocyanate groups may result appropriate to interact chemically with the soap network, modifying the bulk rheology of greases, as have been shown in a previous work [6]. The addition of poly(1,4-butanediol) tolylene 2,4-diisocyanate (PBTDI) to lithium 12-hydroxystearate lubricating greases produces a significant modification of their rheological response. It

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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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has been reported that the effectiveness of such prepolymers to modify the rheology of greases is due to the progress of the reaction between terminal isocyanate groups and the hydroxy group located in the hydrocarbon chain of the lithium 12-hydroxystearate soap. However, the thermo-mechanical conditions involved in lubricating grease processing must be optimized when such reactive polymers are used. The high temperature achieved during processing may increase the reactivity of isocyanate groups or even cause some thermal degradation [7,8]. In a previous work [9], it was shown that PBTDI can be satisfactorily used as rheology modifier of lubricating greases when it was added to the formulation during the final cooling step of grease manufacture. However, the effectiveness of PBTDI as rheology modifier is much lower when the addition takes place during earlier steps of the manufacturing process. This can be explained by some competitive reactions due to either the presence of water or the high temperature applied.

Since the success of grease rheological modification with such prepolymers seems to be associated to both NCO reactivity and polymer physical characteristics, the design and synthesis of polymers with suitable molecular properties for this application should be considered. Other authors have previously studied [10–12] the efficiency of grafting typical elastomeric polymers with carbamate groups, as well as the synthesis of novel polyurethanes for different applications. Urethane prepolymers are isocyanate-tipped macromolecular chains containing urethane groups in their backbone, obtained by reaction of an isocyanate (–NCO) group and a polyol hydroxyl group (–OH). If a stoichiometric excess of diisocyanate is used, the resulting typically diurethane short chains are –NCO terminated. Usually, they have a free isocyanate (NCO) content comprised between 1 and 15 wt%. Urethane prepolymers containing higher free isocyanate contents, between 15 and 30 wt%, are known as isocyanate quasi-prepolymers [13]. In the presence of the isocyanate excess, biurets and allophanates can also be formed [7].

This work deals with the synthesis and further characterization of NCO-terminated prepolymers, prepared from several di and trifunctional polyols and polymeric MDI, in order to evaluate their effectiveness as rheology modifiers of lithium lubricating greases. Particularly, the effects that free NCO content, molecular weight and functionality of the reactive prepolymers exert on the rheological response and microstructure of lubricating greases were studied.

2. Materials and methods

2.1. Materials

12-Hydroxy stearic acid, lithium hydroxide and a naphtenic mineral lubricating oil (density at 20 °C: 916 kg/m^3; kinematic viscosity at 40 °C: 115 mm^2/s) were used to prepare lithium 12-hydroxystearate lubricating greases (14% (w/w) soap). All the components were kindly supplied by Verkol, S.A. (Spain). NCO-terminated prepolymers were synthesized from polymeric 4,4′-diphenyl methane diisocyanate, pMDI, (Dow Chemical, Spain) and different propylene-glycols (Repsol YPF, Spain). The pMDI is a residual component of the synthesis of pure MDI, consisting of a mixture of non-distilled and condensation products resulting from MDI purification. This product consists of monomers and oligomers of MDI as detailed elsewhere [12,14,15], being 2.7 the average functionality. Several polypropylene-glycols, with different average molecular weights and functionalities (see Table 1), were used as received.

Table 1
Molecular characteristics of the polyol samples used for the synthesis of NCO-terminated prepolymers

Polyol	M_n	Functionality
P400/2	400	2
P1000/2	1000	2
P2000/2	2000	2
P4000/2	4000	2
P3000/3	3000	3
P4800/3	4800	3
P6000/3	6000	3

2.2. Synthesis of NCO-terminated prepolymers

Following the methodology described by Bordado and coworkers [12], NCO-terminated prepolymers were synthesized by inducing the reaction between a polyol and an excess (5% molar) of pMDI. Batches of, approximately, 1 kg were prepared by adding the corresponding amounts of polyol and pMDI. The synthesis was carried out in a glass reactor equipped with a stirrer, thermocouple and nitrogen gas inlet system. First of all, pMDI was poured into the reactor, under a nitrogen atmosphere, and heated up to 70 °C. Then, the polyol was added. Inert atmosphere was used to avoid moisture and subsequent formation of urea linkages. This mixture was maintained in oven, at 70 °C for 24 h. Then, prepolymer samples were stored at 5 °C. Prepolymer isocyanate content after synthesis was determined by titration with *N*,*N*′–dibutylamine. The compositions of different prepolymers obtained are shown in Table 2.

2.3. Manufacture of lubricating greases

Processing of greases was performed in a mixing batch reactor (600 g), using an anchor impeller geometry and a rotational speed of 60 rpm. Processing details and procedure have been extensively described elsewhere [16]. Once the saponification was completed, the mixture was heated up to a maximum temperature of 180 °C, in order to induce the phase transition of soap crystallites into a waxy phase, and complete the dehydration process. Afterwards, a controlled cooling ramp down to room temperature was imposed. The addition of NCO-terminated prepolymer was carried out at 90 °C, during the final cooling step, as previously reported [17], inducing the reaction between lithium 12-hydroxystearate and NCO-terminated prepolymers (see Fig. 1). More details on this type of reactions can be found elsewhere [17]. The whole manufacturing process generally occurred over a period of 18 h. A final homogenisation treatment (rotational speed: 8800 rpm; homogenisation

Table 2
Compositions of the NCO-terminated prepolymer samples manufactured for this study

Prepolymer	Polyol	Polyol/MDI molar ratio	Functionality (theoretical)	NCO (wt%) (theoretical)	NCO (wt%) (measured)
P400-MDI	P400/2	1:5	3.4	22.9	21.0
P1000-MDI	P1000/2	1:5	3.4	17.5	16.3
P2000-MDI	P2000/2	1:5	3.4	12.8	11.5
P4000-MDI	P4000/2	1:5	3.4	8.4	2.3
P3000-MDI	P3000/3	1:5	5.1	9.1	7.6
P4800-MDI	P4800/3	1:5	5.1	6.8	5.6
P6000-MDI	P6000/3	1:5	5.1	5.6	4.3

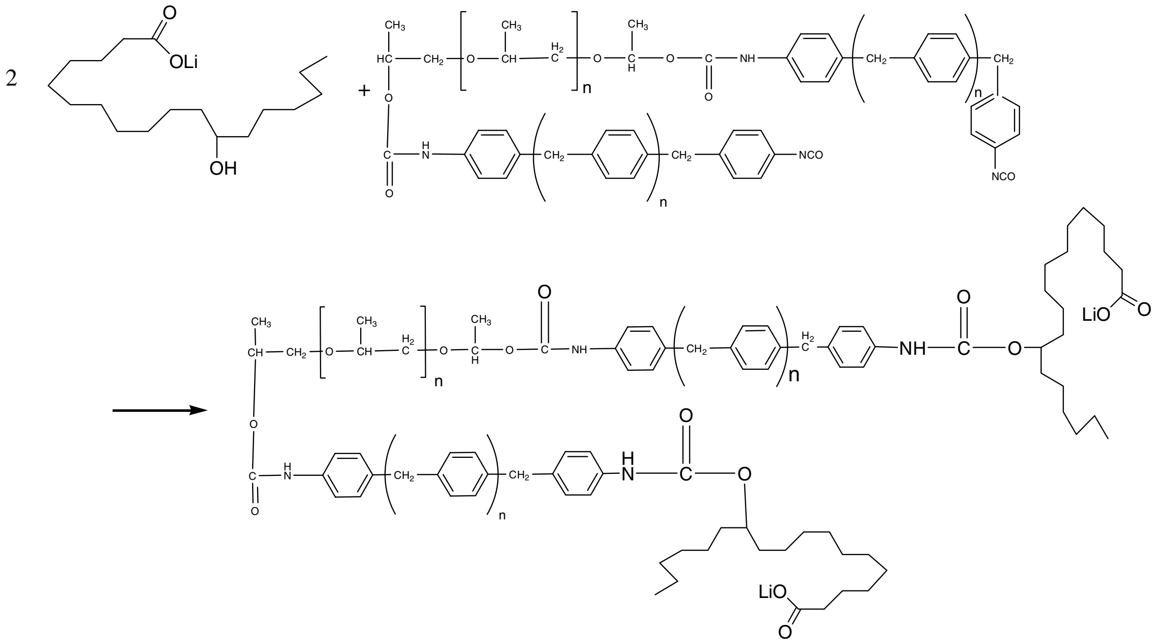

Fig. 1. Main reaction promoted between NCO-terminated prepolymer and lithium 12-hydroxystearate.

time: 15 min), using a rotor-stator turbine (Ultra Turrax T-50, Ika, Staufen, Germany), was applied at room temperature. The different lubricating greases manufactured, with expression of the corresponding additives used, are listed in Table 3.

2.4. Fourier transform infrared spectroscopy (FTIR)

FTIR spectra were obtained with Digilab FTS3500ARX (Varian) apparatus. A small drop from different prepolymer and grease samples was placed between two KBr disks (32×3 mm) and the set placed into an appropriate sample holder. The spectra were obtained from in a wavenumber range of 400–4000 cm^{-1} at 4 cm^{-1} resolution in the transmission mode.

Table 3
Lubricating grease samples manufactured for this study

Greases	Additive (3% w/w)
Reference	Additive-free
A	P400-MDI
B	P1000-MDI
C	P2000-MDI
D	P4000-MDI
E	P3000-MDI
F	P4800-MDI
G	P6000-MDI

2.5. Gel permeation chromatography (GPC)

GPC determinations were performed with a Waters apparatus, equipped with two styragel® HR columns (7.8×300 mm) linked in series, at 35 °C, using $CHCl_3$ as eluent. A Waters 2414 refractive index detector was used. The flow rate was 1.0 mL min^{-1}. 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.

2.6. Differential scanning calorimetry

DSC measurements were performed with a Q-100 TA instrument, using 5–10 mg samples sealed in hermetic aluminium pans. Heating rates of 5 and 10 °C/min, inside a maximum temperature range of −85 to 220 °C, were applied. The sample was purged with nitrogen at a flow rate of 50 mL/min. Calibrations of temperatures and enthalpies were performed with standard Indium.

2.7. *Rheological characterization*

The rheological characterization was carried out in a controlled-strain (ARES, Rheometric Scientific) rheometer, at 25 °C. Small amplitude oscillatory shear (SAOS) tests, inside the linear viscoelasticity region, were carried out in a frequency range comprised between 0.01 and 100 rad/s, using a serrated plate-and-plate geometry (25 mm diameter, 1 mm gap). Strain sweep tests, at the frequency of 1 Hz, were previously performed on each sample to determine the linear viscoelasticity region. All the samples had the same recent past thermal and mechanical history. At least two replicates of each test were carried out on fresh samples.

2.8. *Penetration and mechanical stability tests*

Both unworked and worked penetration indexes were determined according to ASTM D1403 standard, using a Seta Universal Penetrometer, model 17000-2 (Stanhope-Seta), with one-quarter cone geometry. The one-quarter scale penetration values were converted into the equivalent full-scale cone penetration values, as indicated in ASTM D217. The samples were worked in a Roll Stability Tester, model 19400-3 (Stanhope-Seta), according to ASTM D1831 standard. The mechanical stability of grease was then calculated as the difference between worked and unworked penetration values.

2.9. *Atomic force microscopy*

The microstructural characterization of greases was carried out by means of atomic force microscopy (AFM), with a Multimode AFM connected to a Nanoscope-IV scanning probe microscope controller (Digital Instruments, Veeco Metrology Group Inc., Santa Barbara, CA). All images were acquired in the tapping mode, using Veeco Nanoprobe^{TM} tips.

3. Results and discussion

3.1. *NCO-terminated prepolymer characterization*

Synthesized prepolymers, used as additives in grease formulations, as well as reactive materials have been characterized by FTIR, DSC and GPC techniques. The IR spectrum of the polyol used to synthesize NCO-terminated prepolymers (Fig. 2a) displays several characteristic peaks: the first one, at 1109 cm^{-1}, corresponds to the asymmetrical stretching of the unit CH_2–O–CH; the second one, at 2874 of cm^{-1}, is related to the stretching of C–H bonds of the oxymethylene group (O–CH_2); and the last one, at 3447 cm^{-1}, corresponds to the stretching of O–H groups. On the other hand, polymeric MDI presents the main characteristic peak at 2278 cm^{-1}, which corresponds to the stretching of NCO groups (Fig. 2b). The IR spectra of all diisocyanate-terminated prepolymers show similar bands. In this sense, Fig. 2c displays a typical example of IR spectrum. The most important peaks detected are listed in Table 4. The peak that appears at 2259 cm^{-1} is of decisive importance for monitoring the success and evolution of the reaction promoted in grease formulations.

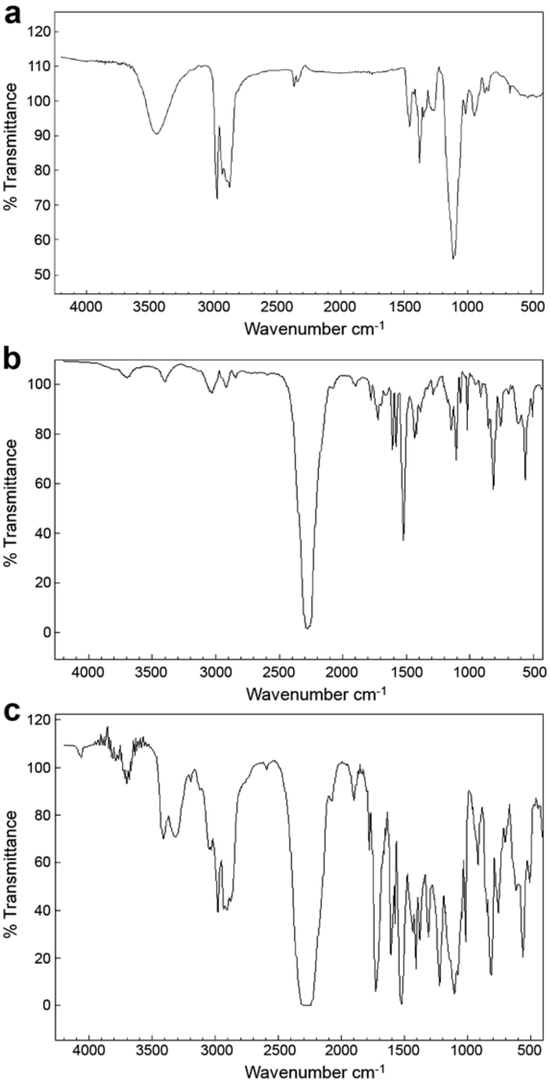

Fig. 2. IR spectra of reagents and prepolymer materials: (a) P400/2, (b) pMDI, and (c) P400-MDI.

Table 4
FTIR characteristic peaks for NCO terminated prepolymers

Functional group	Wavenumber (cm^{-1})
N–H stretching	3312
N–H bending	1527
C═O stretching	1728
C–O stretching	1225
N═C═O stretching	2259
C–O–C streching	1107

DSC thermograms of NCO-terminated prepolymers show just one glass transition. The glass transition temperatures (T_g) for each of the prepolymers studied are listed in Table 5. As expected, T_g's decrease as the average molecular weight of polyol chains increased, due to a higher content in more flexible segments [18].

The number (M_n) and weight (M_w) average molecular weight values of NCO-terminated prepolymers were determined by GPC, using polystyrene standards. M_n, M_w and polydispersity index values for all the prepolymers studied are collected in Table 5. As can be observed, the highest differences in molecular weights in relation to the theoretical values, and the highest polydispersity values, are generally found for prepolymers synthesized from branched polyols, i.e., functionality 3. This fact can be attributed to a partial polymerisation of NCO-terminated prepolymers during the reaction.

Table 5
Molecular weights and glass transition temperatures for the NCO-terminated prepolymer samples studied

Prepolymer	M_n [a]	M_n [b]	M_w [b]	M_w/M_n [b]	T_g (°C) [c]
P400-MDI	1100	1049	1743	1.66	−23
P1000-MDI	1700	1896	2306	1.22	−37
P2000-MDI	2700	3726	6200	1.66	−51
P4000-MDI	4700	9717	16143	1.66	−56
P3000-MDI	4050	14,554	128,066	8.80	−45
P4800-MDI	5850	17,879	113,039	6.32	–
P6000-MDI	7050	12,571	15,668	1.25	–

[a] Theoretical values.
[b] Determinated by GPC relative to poly(styrene) standards.
[c] From DSC measurements.

3.2. DSC and FTIR spectroscopy of greases containing reactive prepolymer

Fig. 3 displays the heat flow curves obtained from DSC measurements for selected greases. As previously reported [16], the grease of reference shows only one endothermic peak at 202 °C, which corresponds to the melting point of lithium 12-hydroxystearate. Grease A displays the same heat flow pattern, showing only the peak corresponding to the soap melting point, although this peak appears broader (see fusion enthalpy values inside Fig. 3), probably due to the new compound generated (see Fig. 1). However, no further peaks related to any other transition of the prepolymer, in the range of temperature studied, are noticed. In this case, DSC is not an adequate technique for detecting the progress of the chemical reaction between prepolymer and lithium 12-hydroxy-stearate. Nevertheless, slightly higher values of fusion enthalpy (ΔH_f) are obtained for greases containing NCO-terminated prepolymers (mean value: 19.13 ± 1.49 J/g), no matter prepolymer molecular weight is, in comparison to that obtained for the additive-free grease (14.27 ± 0.45 J/g).

FTIR spectroscopy is a more appropriate technique to detect the chemical interaction between prepolymer and soap matrix. The reaction between NCO and –OH groups of prepolymer and lithium 12-hydroxystearate, respectively, is confirmed by analyzing the FTIR spectra. Fig. 4 shows selected IR spectra of lubricating greases, obtained 24 h after grease manufacture. As can be observed in Fig. 4a and b, the main differences found in the IR spectrum of grease A and the additive-free grease are related to the presence of the NCO absorption band at 2273 cm^{-1},

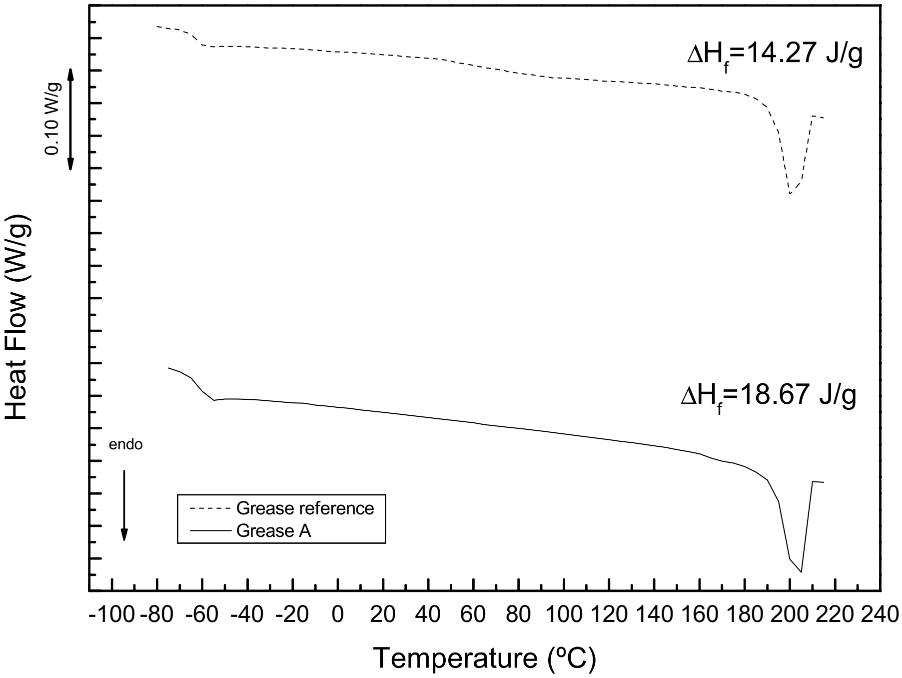

Fig. 3. DSC heat flow curves for selected lubricating greases.

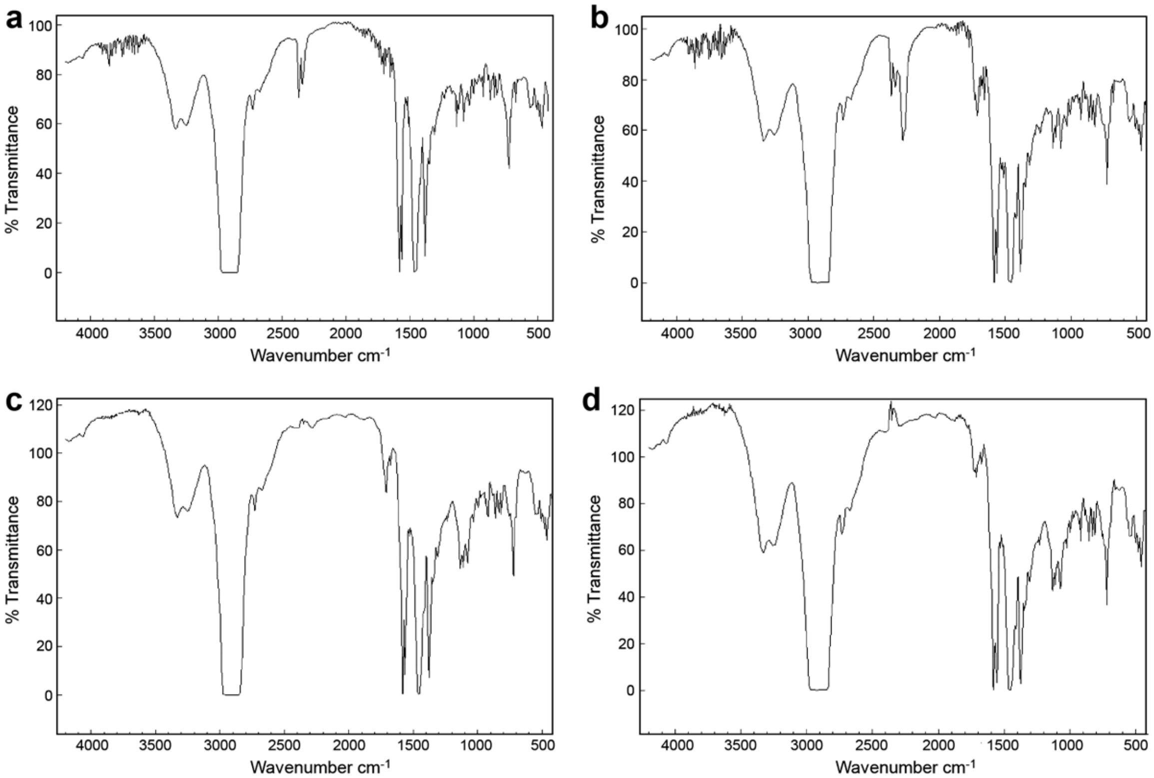

Fig. 4. IR spectra of selected lubricating greases: (a) additive-free grease, (b) grease A, (c) grease D and (d) grease F.

corresponding to the non-reacted prepolymer (or MDI in excess), and the peak at 1717 cm^{-1}, due to the C=O stretching vibration of the urethane group (–NH–CO–O–). This indicates that the prepolymer P400-MDI has only partially reacted with the lithium 12-hydroxystearate. IR spectra for greases B and C (data not shown) are very similar to that shown in Fig. 4b. On the contrary, the absorption band corresponding to NCO groups practically is not

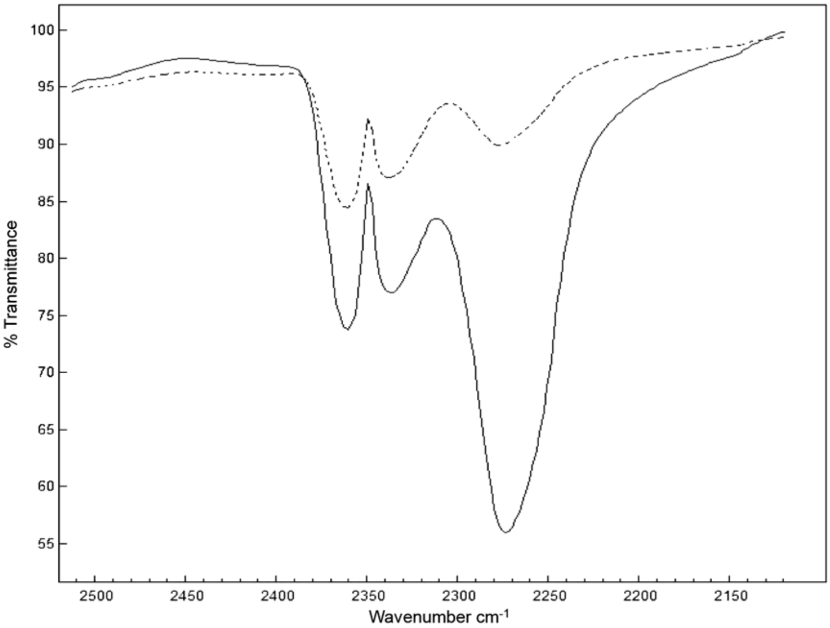

Fig. 5. IR spectra of grease A as a function of grease ageing (———— 24 h; ------- 300 days ageing).

detected in grease D (Fig. 4c), whist, once again, that corresponding to the urethane group is apparent. This fact can be explained taking into account the decrease in free isocyanate content for the same amount of additive (3% w/w), associated to a significantly higher molecular weight (Table 5). Similarly, the free NCO absorption band at 2273 cm^{-1} is not detected in greases with branched prepolymers (Fig. 4d). This means that free NCO groups in prepolymers of higher molecular weights have reacted almost completely after 24 h grease ageing.

Fig. 5 shows an expanded window of the FTIR spectra for grease A, obtained after 24 h and 300 days grease ageing, respectively. As can be observed, the free NCO band progressively vanishes with ageing. This fact is due to the higher content in free NCO for prepolymer P400-MDI. The reactive NCO groups of the prepolymer react with soap –OH groups for several months after grease manufacture. As expected, the rheological response is satisfactorily modified during grease ageing, as will be discussed later (see Fig. 10).

3.3. Rheology of greases

3.3.1. Influence of prepolymer molecular weight

Figs. 6a and 7a show the evolution of the storage (G') and loss (G'') moduli with frequency, within the linear viscoelasticity range, for lubricating greases differing in the prepolymer used as additive, after 24 h grease ageing. Prepolymer concentration in grease formulation was fixed at 3% (w/w). As can be observed, the values of the storage modulus, G', are always significantly higher than those found for the loss modulus, G'', in the whole frequency

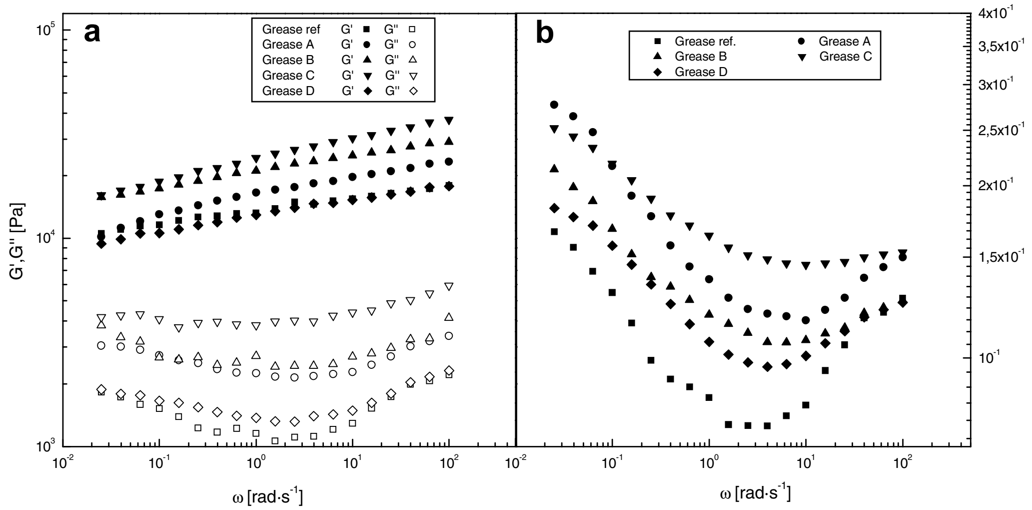

Fig. 6. Frequency dependence of the storage and loss moduli (a) and tanδ (b) for selected lubricating greases, containing linear NCO-terminated prepolymers (3% w/w), at 25 °C.

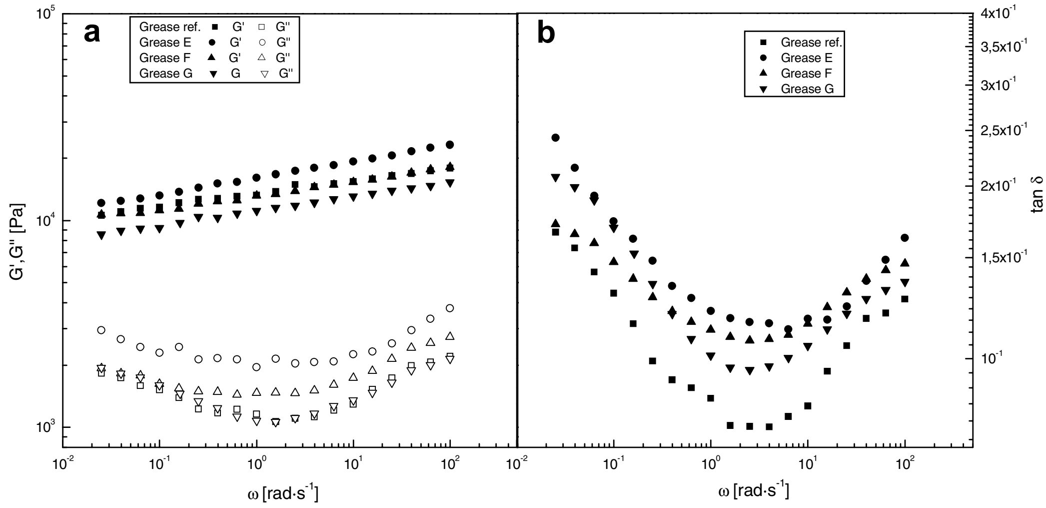

Fig. 7. Frequency dependence of the storage and loss moduli (a) and tanδ (b) for selected lubricating greases, containing branched NCO-terminated prepolymers (3% w/w), at 25 °C.

range studied. Moreover, the so-called "plateau region" is always noticed, where G' slightly increases with frequency and G'' displays a clear minimum. This mechanical spectrum corresponds to the typical evolution of other commercial and model lubricating greases previously studied [19,20]. The most characteristic parameter of this mechanical spectrum is the plateau modulus, G_N^o, defined for polymers as the extrapolation of the contribution of entanglements to G' at high frequencies [21]. It may be considered as a measure of the aggregation of the dispersed structural units or the density of physical entanglements, and, consequently, it is related to the strength of the microstructural network. A short-cut method to estimate G_N^o from the loss tangent can be applied [22]:

$$G_N^o = [G']_{\tan\delta \to \text{minimum}}. \tag{1}$$

From the analysis of Fig. 6a, it can be deduced that grease C shows the largest increment in the values of both viscoelasticity functions in relation to the grease of reference, although it is more important for G'' values. Consequently, as shown in Fig. 6b, which displays the evolution of the loss tangent ($\tan\delta = G''/G'$) with frequency, prepolymer P2000-MDI used as additive confers to the grease (sample C) a significantly more relative viscous response than the rest of prepolymers studied in this work. Slightly poorer modification was achieved by using prepolymer P1000-MDI as additive (grease B). At first sight, this fact seems to indicate that rheology modification is more effective when the prepolymer molecular weight increases. However, as can be deduced from Fig. 6a, much lower or almost negligible influence was observed using prepolymers having both the lowest and the highest molecular weights, greases A and D, respectively. This fact suggests that either NCO groups are not enough in the case of prepolymer P4000-MDI or they have not reacted completely with the hydroxy group located in the hydrocarbon chain of lithium soap in the case of prepolymer P400-MDI. Most of these prepolymers confer to the grease a similar relative elastic response, lower than the grease of reference but higher than grease C, as can be deduced from the values of the loss tangent (Fig. 6b). Similarly, Fig. 7 compares the mechanical spectra of greases with added reactive branched prepolymers, i.e., synthesized using trifunctional polyols of different molecular weight. As can be observed, all these polymers exert a low influence on the rheology of greases, once again more important on G''. Only prepolymer P3000-MDI seems to modify significantly the rheological response (grease E).

According to these results, it can be concluded that rheology modification of greases exerted by NCO-terminated reactive prepolymers is a consequence of the balance between the molecular weight and the number of NCO groups available to react with the hydroxyl group of soap molecules. Thus, if additive concentration is kept constant, P4000-MDI contributes with a low percentage of NCO groups (see Table 2) and, on the contrary, P400-MDI seems to have a non-influencing molecular weight but a significant amount of NCO reactive groups. The effect of branched prepolymers is similar to that shown by P4000-MDI in spite of the higher NCO functionality, since real molecular weights are significantly higher that those obtained with linear polyols (see Table 5).

The effect of prepolymer molecular weight on grease rheology is shown in Fig. 8, where the influence of free NCO content has been isolated. Thus, different greases with the same free NCO molar content were prepared by modifying accordingly the additive concentration. In this case, the values of the linear viscoelasticity functions continuously increase with prepolymer molecular weight, taking into account that the effective concentration is higher for prepolymers with the highest molecular weights. On the other hand, the relative elasticity of greases decreases with this variable in spite of the highest prepolymer concentration (Fig. 8b). At first sight, these data suggest that increasing prepolymer molecular weight results in a more effective rheological modification when the NCO molar

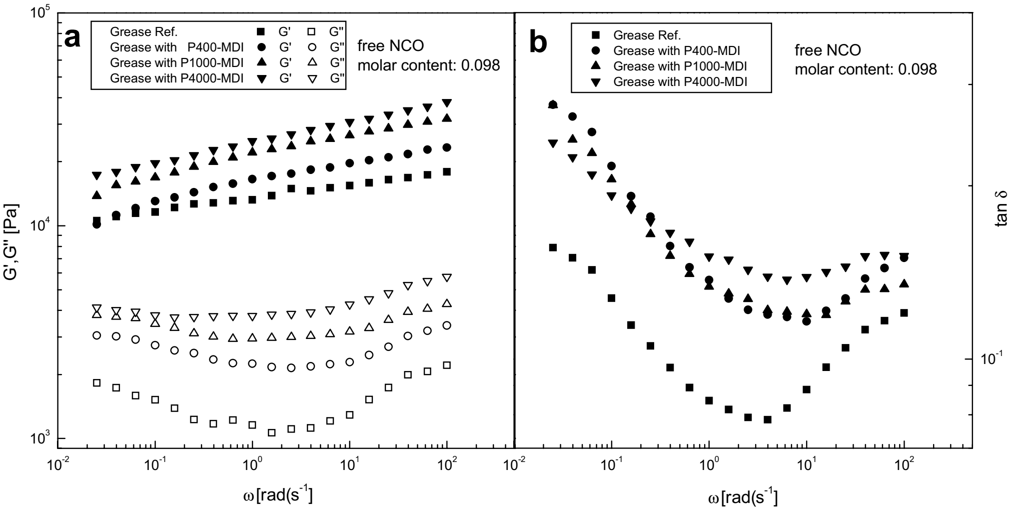

Fig. 8. Frequency dependence of the storage and loss moduli (a) and $\tan\delta$ (b) for selected lubricating greases, containing similar free NCO concentration (0.098 mol) and using different amounts of polymeric additives, at 25 °C.

content is kept constant. However, Fig. 9 shows that increasing polymer molecular weight is not always favourable and the effectiveness depends on the free NCO content. As can be observed, no improvement is found by increasing continuously the length of polyol chain when the total amount of NCO in grease formulation is 0.075 mol. However, no influence of molecular weight is detected below a critical NCO content value, i.e. 0.036 mol, whatever the molecular weight is.

3.3.2. Ageing of greases

The reactivity of polymers with NCO functional groups may be extremely slow in the case of highly viscous media [23]. Thus, preliminary studies [6] showed that the rheological properties of greases with added PBTDI evolve during several months of ageing. As was demonstrated, the effectiveness of a NCO-terminated prepolymer to modify grease rheology is mainly due to NCO reactivity and, consequently, the influence of molecular weight discussed above may change during ageing.

Fig. 10 shows the evolution of the plateau modulus during ageing for selected greases containing 3% w/w of different diisocyanated-terminated prepolymers. G_N^o does not significantly increase during ageing (up to 400 days) for the grease of reference. On the contrary, this modulus increases during several months ageing for all greases containing NCO-terminated prepolymer, which confirms that reaction rate is very slow. The most important increase in G_N^o is observed for grease A during the first 90 days of ageing, then remaining almost constant. This fact can be due to the higher concentration of NCO reactive groups in the bulk prepolymer P400-MDI (see Table 2). These results are corroborated by carrying out FTIR measurements, as shown in Fig. 5, where the progress of the reaction is clearly demonstrated. On the contrary, the increase in G_N^o for greases C and D, containing P2000-MDI and P4000-MDI, respectively, is not so important. In the case of grease C, G_N^o does not increase significantly during the three first months because, as was previously discussed, the rheology modification occurs almost immediately after grease manufacture. On the other hand, the effect of ageing is much less important for greases containing additives that were synthesized using trifunctional polyols.

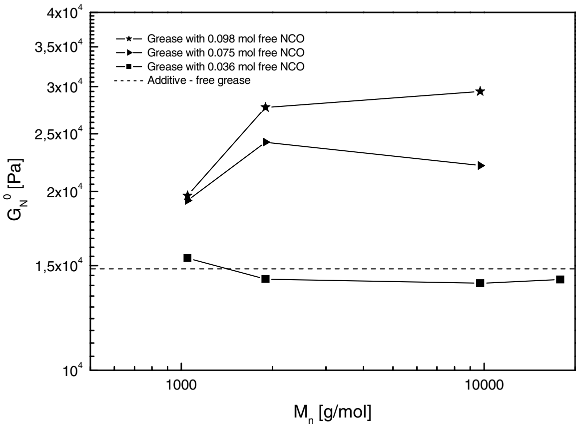

Fig. 9. Evolution of the plateau modulus with prepolymer average molecular weight for different greases, as a function of free NCO molar content.

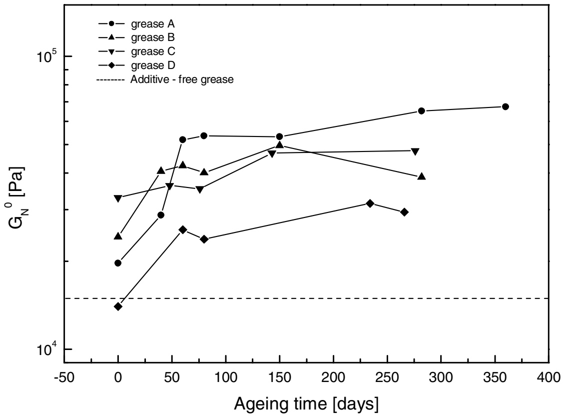

Fig. 10. Evolution of the plateau modulus during grease ageing.

3.3.3. Influence of free NCO content

Fig. 9 shows the evolution of grease plateau modulus with the average molecular weight of the linear prepolymers used to modify the formulation, as a function of free NCO content. Plateau modulus values raise with free isocyanate content (including pMDI excess), more significantly as prepolymer molecular weight increases. As was previously commented, G_N^o values are lower than those obtained for the grease of reference when the NCO amount added to lithium 12-hydroxystearate soap is low enough, i.e., 0.036 mol, no matter prepolymer molecular weight is.

These results confirm that a balance between prepolymer molecular weight and NCO content is necessary to reach optimal grease rheological modification. In this sense, Fig. 11 shows the values of the plateau modulus plotted versus NCO content/prepolymer M_n ratio, both 24 h after grease manufacture and after 70–80 days ageing. As can be observed, after 24 h ageing, the largest rheolog-

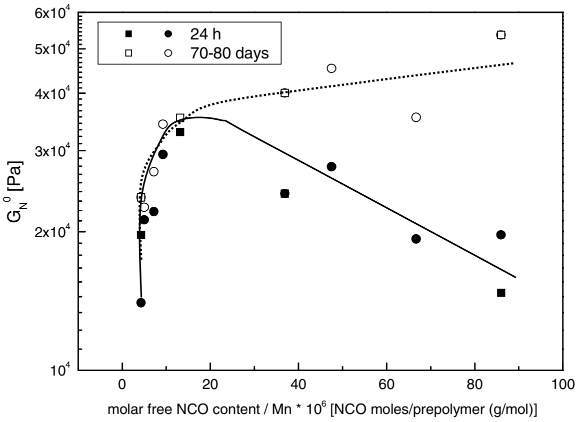

Fig. 11. Evolution of the plateau modulus with the NCO content/prepolymer molecular weight ratio, as a function of grease ageing, for greases containing either 3% w/w of reactive polymer (squares) or variable polymer concentration (circles).

ical modification is achieved at intermediate values of this ratio (around 15–25). Thus, low NCO contents and high polymer molecular weights, and also high NCO contents and low molecular weights should not be selected to yield a large rheological modification, at least just right after grease manufacture. However, this tendency changes with grease ageing. After 70–80 days ageing, due to the slow reactivity of the functional groups, the most effective modification is achieved for the highest values of the NCO content/M_n ratio studied. In addition, it is worth pointing out that ageing does not exert a significant influence on grease rheology below a certain threshold ratio (around 15).

3.3.4. Influence of prepolymer functionality

The influence of prepolymer functionality has been studied on greases containing P4000-MDI (average functionality 3.4), and P3000-MDI (average functionality 5.1). These two prepolymers were selected because they provide very similar NCO contents, for 3% w/w prepolymer concentration, i.e., 0.036 and 0.039 mol, respectively, as well as not very different M_n values. As was previously discussed, these additives do not cause a large initial rheological modification of the grease. This fact can be observed in Fig. 12, where SAOS results are shown for greases containing one of these prepolymers, 24 h after their manufacture. Thus, P3000-MDI prepolymer provides a slightly larger rheological modification during the first days of ageing (grease E), mainly in the viscous component (G''). On the contrary, after a long period of ageing (300 days), once most of the NCO reactive groups have reacted with the soap network, the linear prepolymer (P4000-MDI) produces a higher modification in G' than P3000-MDI

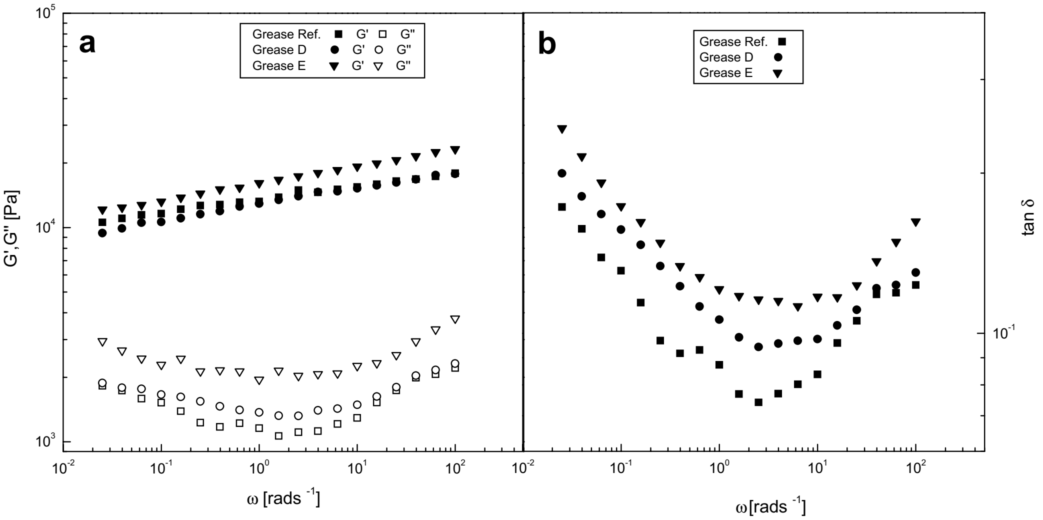

Fig. 12. Frequency dependence of the storage and loss moduli (a) and tan δ (b) for selected lubricating greases, containing NCO-terminated polymers with different functionalities, at 25 °C (24 h after grease manufacture).

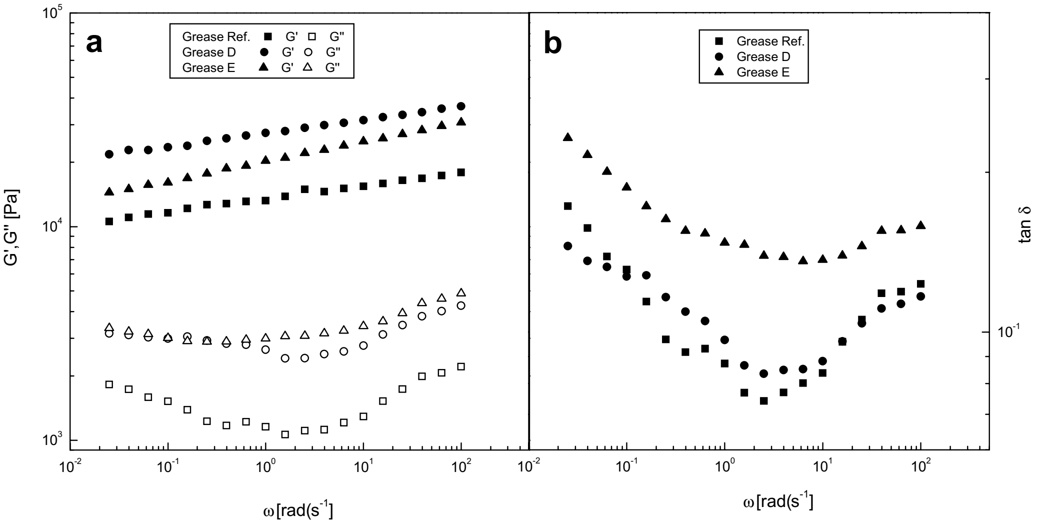

Fig. 13. Frequency dependence of the storage and loss moduli (a) and tan δ (b) for selected lubricating greases, containing NCO-terminated polymers with different functionalities, at 25 °C (300 days after grease manufacture).

branched prepolymer, although G'' values are almost identical (Fig. 13a). This can be attributed to larger polymer chain flexibility in the case of P4000-MDI, yielding a more elastic material (Fig. 13b), as was suggested for curing reactions of NCO-terminated polyurethanes with different hard/soft segments for adhesives applications [18].

3.4. AFM observations

Generally, the microstructure of lithium lubricating greases consists of a fine dispersion of the crystallized thickener in the mineral oil, usually in the form of long, twisted and well tangled fibres [2]. These fibres arrange themselves to form a characteristic microstructure due to the balance of forces between colloidal particles and oil medium, depending on soap concentration as well as nature and viscosity of the mineral oil [20]. Traditionally, the analysis of grease microstructure has been developed through TEM and SEM techniques. The most common criticism associated to SEM or TEM observations is that both techniques are vacuum based, and grease sample must be submitted to either a freezing treatment or oil removing, thus distorting the original microstructure. On the contrary, the advantage of AFM technique is that grease samples do not need to be perturbed, since the experiments can be carried out under atmospheric pressure [9]. Fig. 14(a–e) show AFM micrographs for selected lithium greases with added NCO-terminated prepolymers, and

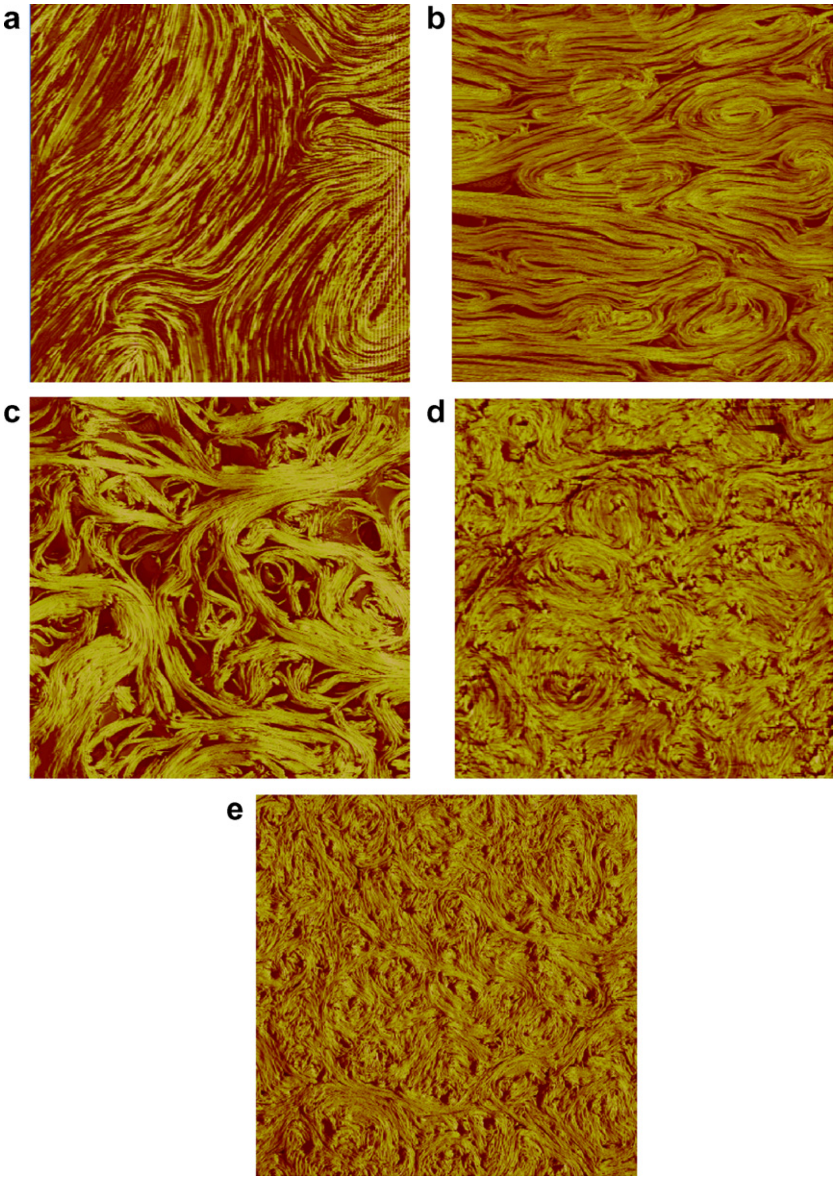

Fig. 14. AFM photomicrographs (window size always corresponds to 10 μm) for selected lubricating greases: (a) additive-free; (b) grease A, ageing: 24 h; (c) grease A, ageing: 300 days, (d) grease D, ageing: 300 days, (e) grease with 0.098 mol free NCO (P4000-MDI).

compared to the additive-free formulation. The main difference found in the additive-free microstructure is that long and not very entangled fibres with large length/width ratios are noticed (Fig. 14a). On the contrary, much more twisted and entangled fibres appear in the microstructure of greases with added NCO-terminated prepolymers. Especially dramatic is the case of grease A, after 300 days ageing, where fibres are clearly more agglomerated (Fig. 14c), giving rise to larger hollow spaces among them, where oil is trapped. The same sponge-type microstructure was detected by SEM observations for a grease formulation containing another similar reactive prepolymer as additive [6]. Intermediate morphology between those obtained in Fig. 14a and c, respectively, is shown by grease A, after 24 h ageing (see Fig. 14b). This fact corroborates the hypothesis that the agglomeration of fibres and the development of a sponge-type microstructure are associated to the progress of the reaction between the NCO-terminated additive and the lithium 12-hydroxystearate [6]. A higher density of fibres and not so agglomerated is noticed for grease D (Fig. 14d), which contains a high-molecular weight prepolymer (P4000-MDI), which may be associated to the higher prepolymer molecular weight. Very similar microstructure is found by increasing P4000-MDI concentration to reach the same free NCO molar content than in grease A (Fig. 14e).

3.5. Mechanical stability of greases

From a tribological point of view, a lubricating grease sample should be physically and chemically stable during operation in a bearing. In this work, the mechanical stability has been simulated through the traditional penetration measurements before and after the standardized roll-stability test. Table 6 shows the penetration values obtained for unworked and worked selected lubricating greases samples. As a general rule, greases are considered stable to the continuous shear of rolling elements when the variation of penetration before and after the test is around zero. As can be observed in Table 6, the lubricating greases samples studied show unworked penetration values which correspond to a NLGI grade 1. Grease A and C show a good mechanical stability similar to that shown by the additive free formulation, with a variation in the penetration index slightly lower that zero (around −10 dmm). In the case of Grease B and D, penetration indexes show rather large negative increment after grease working, which was previously attributed to an incomplete homogenisation [16]. As a consequence, the roll-stability test favours a better dispersion, yielding a lower penetration value after working. Furthermore, mechanical stability is also affected by sample ageing. Table 7 shows penetration values for selected greases obtained after 9 months ageing. As can observed, and in concordance with the rheological results previously discussed, all the formulations, and particularly Grease A, show lower unworked penetration values than those obtained after 24 h grease ageing, which correspond to an increase in the NLGI grade from 1 to 3. These results can be explained, once again, taking into account the progress of the reaction between free NCO groups and hydroxyl groups of the soap matrix. However, worked penetration values are significantly higher than those shown in Table 6. This is related to a poorer sample mechanical stability after 9 months ageing. Consequently, it may be deduced that microstructures induced by reactive NCO-terminated prepolymers show a higher shear dependence, which seems to be dampened by increasing prepolymer molecular weight (see Table 7). Therefore, further work focused on the mechanical and tribological behaviours of these greases, as well as on their thermal dependence, is needed to test the real applicability of these novel formulations.

Table 6
Values of penetration for different unworked and worked lubricating greases, after 24 h ageing

Greases	Unworked penetration (dmm)	Worked penetration (dmm)	Penetration variation (dmm)
Reference (additive-free)	331.5	325.3	−6.2
A	334.0	325.0	−9.0
B	295.6	254.0	−41.6
C	315.4	304.9	−10.5
D	317.9	291.9	−26.0

Table 7
Values of penetration for different unworked and worked lubricating greases, after 300 days ageing

Greases	unworked penetration (dmm)	worked penetration (dmm)	penetration variation (dmm)
A	239.8	353.2	113.4
B	304.9	347.8	42.9
C	275.1	323.5	48.4
D	329.0	334.6	5.6

4. Conclusions

The rheological behaviour of lithium 12-hydroxystearate lubricating greases may be satisfactorily modified by adding reactive diisocyanate-terminated prepolymers synthesized from di and trifunctional polyols and polymeric MDI. The effectiveness of such prepolymers to modify the rheology of greases is related to the progress of the reaction between terminal isocyanate groups and the hydroxy group located in the hydrocarbon chain of the lithium 12-hydroxystearate soap. However, their performance as additive is highly dependent on both free NCO content and molecular weight. Thus, the experimental results obtained confirm that it is necessary a balance between prepolymer molecular weight and NCO content to yield optimal rheological modification of lithium greases. Moreover, this balance is modified during ageing, due to the progress of the reaction promoted. The most important evolution of the rheological functions during ageing is observed for greases with high number of free NCO reactive groups in the reactive bulk. Rheological modification is more important at intermediates values of NCO content/prepolymer M_n ratio for a few days after grease manufacture. On the contrary, NCO content is predominant after a long period of ageing, and, consequently, the most effective modification is achieved for the highest ratio values studied. Finally, after a long period of ageing, linear prepolymers yield a larger rheological modification than trifunctional branched polyols, in spite of their lower functionality.

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References

[1] Gow G. Lubricating grease. In: Mortier RM, Orszulik ST, editors. Chemistry and technology of lubricants. London: Blackie Academic & Professional; 1997. p. 306–19.
[2] NLGI. NLGI lubricating greases guide. Kansas City, MO: National Lubricating Greases Institute; 1994.
[3] Al- Sammerral V. J Appl Polym Sci 1986;31:1–6.
[4] Verstrate G, Struglinski MJ. ACS Symp Ser 1991;462:256–72.
[5] Kernizan CF, Todd PR, Bartlett ME. NLGI Spokesman 2002;66:8–15.
[6] Moreno G, Valencia C, de Paz MV, Franco JM, Gallegos C. Ind Eng Chem Res 2006;45:4001–10.
[7] Lapprand A, Boisson F, Delolme F, Méchin F, Pascault JP. Polym Degrad Stabil 2005;90:363–73.
[8] Yang WP, Macosko CW, Wellinghoff T. Polymer 1986;27:1235–40.
[9] Moreno G, Valencia C, de Paz MV, Franco JM, Gallegos C. Chem Eng Process 2008;47:528–38.
[10] Ding RY, Xin Z, Gao Y, Yin J, Costa G. J Polym Sci Pt B: Polym Phys 2003;41:387–402.
[11] Garçon R, Clerk C, Gesson JP, Bordado J, Numes T, Caroço S, et al. Carbohydr Polym 2001:123–7.
[12] Daniel da Silva AL, Martin-Martinez JM, Moura Bordado JC. J Int Adhes Adhes 2006;26:355–62.
[13] Szycher M. Szycher's handbook of polyurethanes. London: CRC Press; 1999.
[14] Woods G. The ICI polyurethane book. 2nd ed. New York: Wiley & Sons; 1990.
[15] Frazier CE, Ni JW. J Int Adhes Adhes 1998;18:81–7.
[16] Delgado MA, Sánchez MC, Valencia C, Franco JM, Gallegos C. Chem Eng Res Des 2005;83:1085–92.
[17] Anzuino G, Pino A, Rossi O, Polo Friz L. J Polym Sci Part A: Polym Chem 1975;13:1657–66.
[18] Sebenik U, Krajnc M. J Int Adhes Adhes 2007;27:527–35.
[19] Madiedo JM, Franco JM, Valencia C, Gallegos C. J Tribol 2000;122:590–6.
[20] Delgado MA, Valencia C, Sánchez MC, Franco JM, Gallegos C. Ind Eng Chem Res 2006;45:1902–10.
[21] Baumgaertel M, De Rosa ME, Machado J, Masse M, Winter HH. Rheol Acta 1992;31:78–82.
[22] García Morales JA, Franco JM, Valencia C, Sánchez MC, Gallegos C. J Ind Eng Chem 2004;10:368–78.
[23] Martín-Alfonso MJ, Partal P, Navarro FJ, García-Morales M, Gallegos C. Eur Polym J 2008;44:1451–61.