

# Rheology of Lubricating Greases Modified with Reactive NCO-Terminated Polymeric Additives

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**ABSTRACT:** A comprehensive rheological characterization of lithium lubricating greases modified with NCO-terminated polymers has been performed in this work, with special emphasis on the effect of temperature. With this aim, NCO-terminated polymers were prepared from several di- and tri-functional polyols and polymeric MDI. Afterwards, the reaction between terminal isocyanate groups and 12-hydroxystearate lithium soap, used as thickener for lubricating grease formulations, was promoted. Transient and steady-state viscous flow, rheo-destruction and stress relaxation tests were performed on the different samples studied. In this sense, the influence that temperature, free NCO content, molecular weight, and functionality of the reactive polymers exert on the rheological response of lubricating greases was analyzed.

The most important rheological modification was achieved by using the lowest molecular weight polymer. In general, NCO-terminated polymers significantly dampen the influence of temperature on the rheological functions of the additive-free lubricating grease. In some cases, the viscosity and/or viscoelastic functions even increase with temperature, especially in formulations with residual free NCO groups. Several experimental flow problems, such as fracture and sample expelling from the measuring tool, are generally found, more frequently in formulations with high NCO content. © 2010 Wiley Periodicals, Inc., *J Appl Polym Sci* 118: 693–704, 2010

**Key words:** NCO-terminated polymer; reactive polymer; lubricating grease; rheology; transient flow; viscoelasticity

## INTRODUCTION

Lubricating greases are semi-solid colloidal dispersions of a thickening agent (usually a metal soap) in a lubricant liquid (mineral or synthetic oil). Greases are the preferred lubricants in hard-to-reach places, for mechanically rubbing or dynamic systems. Many important functional properties such as their ability to flow under external forces, mechanical stability under shearing, thermal susceptibility, dripping and spattering, etc., depends on the nature of their components and the presence of some performance additives.<sup>1,2</sup> Among these additives, polymers are frequently used to improve some specific properties or characteristics of lubricating greases, such as dropping point, appearance, tackiness, water resistance, sealing, and bleeding. Besides these performance characteristics, the addition of polymers to grease formulations largely influences the rheological behavior of these products.<sup>3–5</sup> In general, polymers are often used as supplements to the traditional

thickening agents, to either decrease the thickener content, by keeping constant the consistency, i.e., the NLGI grade, or increase the consistency of greases for some specific applications, like high-speed bearings where leakage and sealing are particular concerns.<sup>2</sup>

A new generation of reactive polymeric additives, consisting in polyols functionalized with terminal isocyanate groups (NCO) that interact chemically with the soap network, has been proposed in previous studies.<sup>6–8</sup> The addition of NCO-terminated polymers to lithium 12-hydroxystearate lubricating greases produces a significant rheological modification. It has been demonstrated that the effectiveness of these polymers 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. This modification is similar to that achieved with nonreactive polymers of much higher molecular weight.<sup>6</sup> Moreover, the effect of molecular weight and functionality of NCO-terminated polymers on the rheological modification of greases has been reported.<sup>8</sup> Experimental results obtained have confirmed that it is necessarily a balance between polymer molecular weight and NCO content to yield a significant rheological modification of lithium greases, although this balance is

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modified during ageing, due to the progress of the reaction promoted, which follows an extremely slow kinetics. However, the study of this rheological modification has been mainly limited to small-amplitude oscillatory shear (SAOS) experiments inside the linear viscoelastic range. In this work, a comprehensive rheological characterization, including both viscous flow and viscoelastic behaviors, of lithium lubricating greases modified with NCO-terminated polymers of different molecular weight and functionality, has been performed. Special emphasis has been placed on the effect of temperature.

## MATERIALS AND METHODS

### Materials

12-hydroxy stearic acid, lithium hydroxide, and a naphthenic mineral lubricating oil (density at 20°C: 916 kg/m<sup>3</sup>; kinematic viscosity at 40°C: 115 mm<sup>2</sup>/s) were used to prepare lithium 12-hydroxystearate lubricating greases [14% (w/w) soap]. All the components were supplied by Verkol, S.A. (Spain). NCO-terminated polymers were synthesized from polymeric 4,4'-diphenyl methane diisocyanate, pMDI, (Dow Chemical, Spain) and different polypropylene-glycols supplied by Repsol YPF (Spain). The pMDI is a residual component of the synthesis of pure MDI, consisting of monomers and oligomers of MDI as detailed elsewhere,<sup>9</sup> being 2.7 the average functionality. Several polypropylene-glycols, with different average molecular weights (400, 3000, and 4000 g/mol), named P400, P3000, and P4000, respectively, and linear (functionality 2 for P400 and P4000) or branched (functionality 3 for P3000) molecular structures, were used as received. The synthesis of NCO-terminated polymers was followed according to the methodology described by Daniel da Silva et al.<sup>10</sup> NCO-terminated polymers were synthesized by inducing the reaction between the polyol and an excess (5% molar) of pMDI. Further details can be found elsewhere.<sup>8,10</sup> Free NCO contents and polymer functionalities for the different NCO terminated

**TABLE I**  
Molecular Characteristics of NCO-Terminated Polymers Used as Additives in the Lubricating Grease Formulations Studied

Polymer	Functionality <sup>a</sup>	$M_n^b$	$M_w^b$	$M_w/M_n^b$	NCO (% wt)
P400-MDI	3.4	1049	1743	1.66	21.0
P4000-MDI	3.4	9717	16143	1.66	2.3
P3000-MDI	5.1	14554	128066	8.80	7.6

<sup>a</sup> Theoretical values referred to free NCO in the polymer chain (taking into account pMDI functionality).

<sup>b</sup> Determinated by GPC relative to poly(styrene) standards.

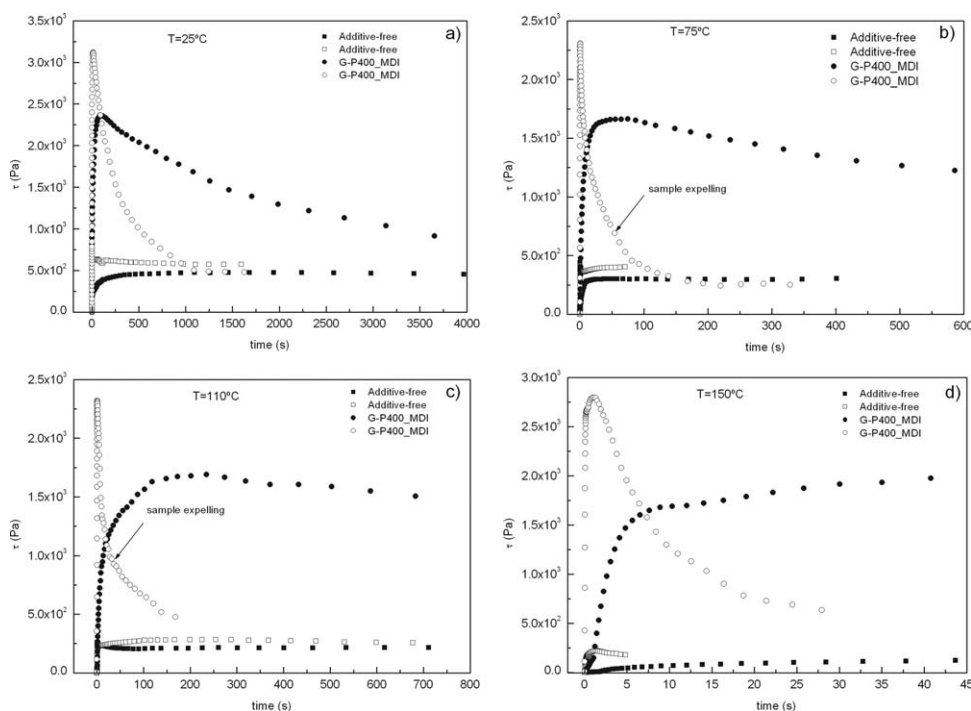
**TABLE II**  
Lubricating Grease Samples Manufactured for This Study

Grease	Additive	% w/w	NCO molar content/kg grease
Additive-free	–	–	–
G-P400-MDI	P400-MDI	3.00	0.163
G-P4000-MDI	P4000-MDI	3.00	0.060
G-P4000-MDI-HC	P4000-MDI	8.45	0.163
G-P3000-MDI	P3000-MDI	3.00	0.065

polymers synthesized are shown in Table I. Polymer isocyanate content after synthesis was determined by titration with *N,N'*-dibutylamine.<sup>11</sup> Lubricating greases were manufactured according to the procedure described by Moreno et al.<sup>8</sup> NCO-terminated polymers were included in grease formulations as additives, at a fixed concentration (3% w/w), excepting when the same free NCO molar content was evaluated. The different lubricating grease samples prepared, with expression of the corresponding additives and concentrations used, are listed in Table II. Polymer addition protocol was previously optimized,<sup>7</sup> to favor the reaction between lithium 12-hydroxystearate and NCO-terminated polymers.

### Rheological tests

Rheological measurements were carried out in both controlled-stress (RS150, ThermoHaake, Germany) and controlled-strain (ARES, Rheometric Scientific, UK) rheometers, using plate-plate geometries (25 mm and 35 mm diameters, 1 mm gap), with rough surfaces (average roughness value: 0.4 mm) to avoid wall-slip phenomena.<sup>12</sup> Viscous flow measurements were carried out in both types of rheometers, in a range of 10<sup>-5</sup>–120 s<sup>-1</sup>, according to a step-ramp of increasing shear rates or stresses (6 min per point). Transient shear flow (stress growth) and stress relaxation measurements were performed with the ARES rheometer. Transient shear stress experiments were done at different constant shear rates (0.0125, 0.1, 1, and 10 s<sup>-1</sup>). Stress relaxation curves were obtained at different constant strains comprised between 0.05 and 150%. Rheo-destruction tests were carried out in the RS150 rheometer by applying a constant stress in oscillatory shear, at 1 Hz, inside the linear viscoelastic regime and a subsequent stress outside the linear viscoelastic range. Afterwards, the recovery was evaluated by restoring the stress inside the linear viscoelastic region. Rheological characterization of lubricating greases was carried out at different temperatures, comprised between 25 and 150°C. At least two replicates of each test were carried out on fresh samples.



**Figure 1** Shear stress-growth curves for selected polymer-modified lubricating greases (different free NCO molar content), at different shear rates and temperatures (filled symbols:  $0.0125 \text{ s}^{-1}$ ; open symbols:  $1 \text{ s}^{-1}$ ).

### Gel permeation chromatography (GPC)

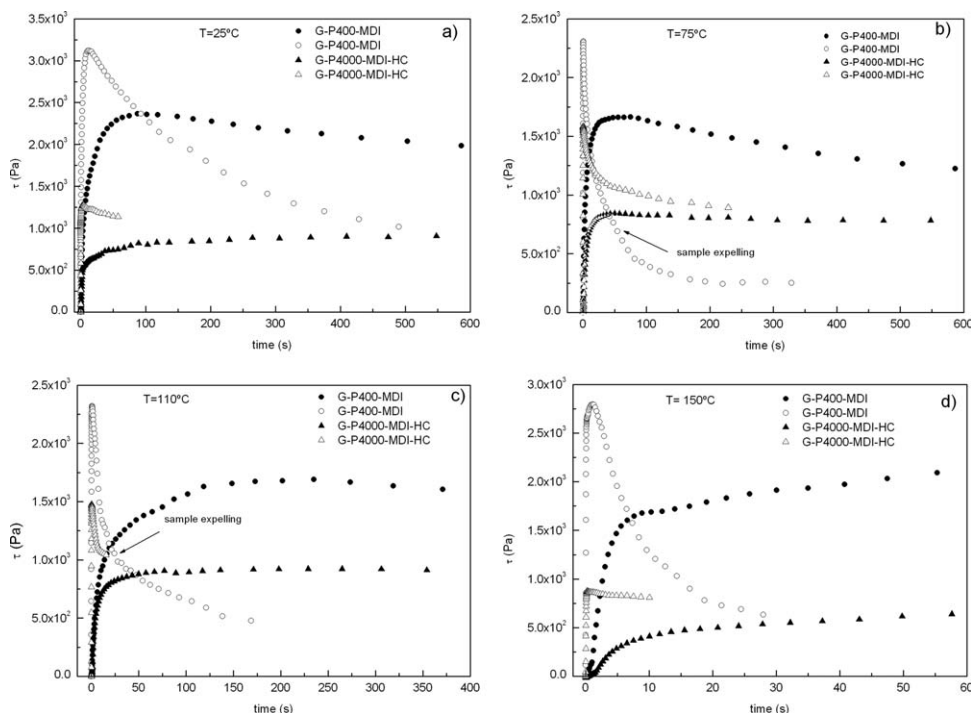
GPC determinations were performed with a Waters apparatus, equipped with two styragel<sup>®</sup> HR columns ( $7.8 \times 300 \text{ mm}$ ) linked in series, at  $35^\circ\text{C}$ , using  $\text{CHCl}_3$  as eluent. A Waters 2414 refractive index detector was used. The flow rate was  $1.0 \text{ mL min}^{-1}$ . 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. Molecular weight data for all the polymers used as additives are collected in Table I.

## RESULTS AND DISCUSSION

### Transient viscous flow

The transient viscous flow behavior of the lubricating greases studied was investigated by means of stress growth experiments at constant shear rate. Stress-growth results of lubricating greases have been related to shear-induced microstructural changes,<sup>13,14</sup> and linked to lubricant performance, especially during the start-up process of the lubricated contact. Thus, grease elastic deformation, thickener particles reversible orientation, and the final irreversible dispersion of these particles in the oil can be attributed to progressive changes in the structure of the grease when it has been subjected to the friction process.<sup>15</sup> Taking into account

these different stages, transient shear tests may be a useful rheological tool to analyze these phenomena. For instance, as previously reported,<sup>13,16</sup> the energy associated to the deformation process of the grease film in a mixed friction regimen can be estimated by performing rheological time-dependent experiments. Figures 1 and 2 show transient flow curves for selected lubricating greases, obtained at different temperatures and shear rates. The transient stress evolution is typical of thixotropic colloidal materials,<sup>17</sup> and very similar to that previously reported for other additive-free lithium lubricating greases.<sup>14</sup> Thus, two main regions are noticed, resulting from the well-known nonlinear viscoelastic response of these lubricating greases. The first region, comprised between the onset of the transient test and the maximum stress reached, or stress overshoot ( $\tau_{\text{max}}$ ), is mainly due to the predominant elastic response of lubricating greases, which extent depends on the shear rate applied on the sample. Then, once the stress overshoot is reached, a stress decay down to a steady-state value is observed. This decay is related to the microstructural breakdown of the lubricating grease three-dimensional network. Obviously, the characteristic times and stress values in these curves are dependent on shear rate and temperature. Tables III–VI show the values of some relevant characteristic parameters, derived from the analysis of these stress growth curves, i.e., stress overshoot ( $\tau_{\text{max}}$ ), equilibrium or steady-state stress value ( $\tau_{\text{eq}}$ ), and elapsed time necessary to reach the stress overshoot



**Figure 2** Shear stress-growth curves for selected polymer-modified lubricating greases (identical free NCO molar content), at different shear rates and temperatures (filled symbols:  $0.0125 \text{ s}^{-1}$ ; open symbols:  $1 \text{ s}^{-1}$ ).

( $t_{\max}$ ), for all the samples studied, as a function of shear rate and temperature. In general, lubricating greases rheological characterization presents several experimental flow problems widely described in the existing literature for a variety of materials, such as wall-slip, shear-banding, fracture, sample expelling

from the measuring tool, etc.<sup>18–23</sup> These problems have been already reported in some detail for lubricating greases.<sup>12,24,25</sup> Wall-slip phenomena have been avoided by using grooved geometries but, on the contrary, such geometries may favor the occurrence of fracture and subsequent sample expelling from

**TABLE III**  
Stress-Growth Parameters, at  $0.0125 \text{ s}^{-1}$  for the Lubricating Grease Samples Studied as a Function of Temperature

Grease		$\tau_{\max}$ (Pa)	$\tau_{\text{eq}}$ (Pa)	$t_{\max}$ (s)	$S^+$
$T = 25^\circ\text{C}$	Additive-free	478	423	1680	0.13
	G-P400-MDI	2366	398 <sup>a</sup>	82	6.0
	G-P4000-MDI	494	393 <sup>a</sup>	115	0.26 <sup>a</sup>
	G-P4000-MDI-HC	908	908	309	1.3
	G-P3000-MDI	551	357	474	0.54
$T = 75^\circ\text{C}$	Additive-free	302	300 <sup>a</sup>	38	0.01 <sup>a</sup>
	G-P400-MDI	1652	789	74	1.1
	G-P4000-MDI	615	367	19	0.68
	G-P4000-MDI-HC	843	757	19	0.11
	G-P3000-MDI	630	495	28	0.27
$T = 110^\circ\text{C}$	Additive-free	235	216	3	0.09
	G-P400-MDI	1691	1227	48	0.38
	G-P4000-MDI	528	274	62	0.92
	G-P4000-MDI-HC	906	906	28	0.09
	G-P3000-MDI	548	338	70	0.62
$T = 150^\circ\text{C}$	Additive-free	184	184	91	0.003
	G-P400-MDI	2840	1974 <sup>a</sup>	85	0.44 <sup>a</sup>
	G-P4000-MDI	353	330	125	0.07
	G-P4000-MDI-HC	789	557	63	0.42
	G-P3000-MDI	372	300	80	0.24

<sup>a</sup> Nonequilibrium values, due to significant fracture.

**TABLE IV**  
Stress-Growth Parameters, at  $0.01 \text{ s}^{-1}$  for the Lubricating Grease Samples Studied as a Function of Temperature

Grease		$\tau_{\max}$ (Pa)	$\tau_{\text{eq}}$ (Pa)	$t_{\max}$ (s)	$S^+$
$T = 25^\circ\text{C}$	Additive-free	461	460	1410	0.002
	G-P400-MDI	2959	778	13	2.8
	G-P4000-MDI	507	393	21	0.29
	G-P4000-MDI-HC	1076	974	30	0.10
	G-P3000-MDI	578	462	49	0.25
$T = 75^\circ\text{C}$	Additive-free	395	341 <sup>a</sup>	1.8	0.16 <sup>a</sup>
	G-P400-MDI	2138	829 <sup>a</sup>	4.2	1.6 <sup>a</sup>
	G-P4000-MDI	765	418	1.5	0.83
	G-P4000-MDI-HC	1221	835	2.0	0.46
	G-P3000-MDI	716	411	1.6	0.74
$T = 110^\circ\text{C}$	Additive-free	184	184	91	0.003
	G-P400-MDI	2531	836 <sup>a</sup>	6.9	2.0 <sup>a</sup>
	G-P4000-MDI	762	485 <sup>a</sup>	1.9	0.57 <sup>a</sup>
	G-P4000-MDI-HC	1050	833	3.1	0.26
	G-P3000-MDI	650	584	3.4	0.11
$T = 150^\circ\text{C}$	Additive-free	204	185	7.0	0.11
	G-P400-MDI	2936	2580 <sup>a</sup>	11	0.14 <sup>a</sup>
	G-P4000-MDI	446	390	8.9	0.14
	G-P4000-MDI-HC	877	843 <sup>a</sup>	31	0.04 <sup>a</sup>
	G-P3000-MDI	411	308	8.3	0.34

<sup>a</sup> Nonequilibrium values, due to significant fracture.

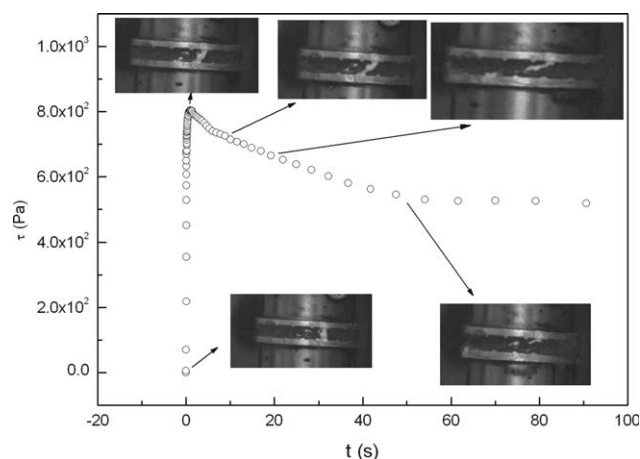
**TABLE V**  
Stress-Growth Parameters, at  $1 \text{ s}^{-1}$  for the Lubricating Grease Samples Studied as a Function of Temperature

Grease		$\tau_{\max}$ (Pa)	$\tau_{\text{eq}}$ (Pa)	$t_{\max}$ (s)	$S^+$
$T = 25^\circ\text{C}$	Additive-free	635	586	55	0.08
	G-P400-MDI	3120	482	13	5.5
	G-P4000-MDI	857	538	0.77	0.59
	G-P4000-MDI-HC	1272	1162	0.99	0.09
	G-P3000-MDI	698	580	2.6	0.20
$T = 75^\circ\text{C}$	Additive-free	443	371	0.15	0.20
	G-P400-MDI	2308	690	0.56	2.3
	G-P4000-MDI	976	386	0.20	1.5
	G-P4000-MDI-HC	1586	898	0.23	0.77
	G-P3000-MDI	973	448	0.20	1.12
$T = 110^\circ\text{C}$	Additive-free	256	235	0.24	0.09
	G-P400-MDI	2320	972	0.61	1.4
	G-P4000-MDI	927	603	0.18	0.54
	G-P4000-MDI-HC	1478	1042	0.21	0.42
	G-P3000-MDI	856	611	0.27	0.40
$T = 150^\circ\text{C}$	Additive-free	219	188	1.4	0.17
	G-P400-MDI	2796	632	0.77	3.4
	G-P4000-MDI	675	545	0.26	0.24
	G-P4000-MDI-HC	826	815	0.36	0.01
	G-P3000-MDI	579	435	0.53	0.33

the gap.<sup>25,26</sup> Shear fracture may be noticed from a significant change in the slope of the transient stress decay, and, sometimes, through visual observations. Figure 3 illustrates shear fracture in a sequence of different steps. Thus, a nonuniform velocity gradient can be observed after 15–18 s shearing time, although, in most cases, a significant fracture of the sample only appears once the steady-state is reached. On the contrary, in other cases, shear fracture makes impossible to reach equilibrium stress

**TABLE VI**  
Stress-Growth Parameters, at  $10 \text{ s}^{-1}$  for the Lubricating Grease Samples Studied as a Function of Temperature

Grease		$\tau_{\max}$ (Pa)	$\tau_{\text{eq}}$ (Pa)	$t_{\max}$ (s)	$S^+$
$T = 25^\circ\text{C}$	Additive-free	908	719	0.31	0.26
	G-P400-MDI	4018	1446	0.24	1.8
	G-P4000-MDI	1086	757	0.08	0.43
	G-P4000-MDI-HC	2138	2090	0.17	0.02
	G-P3000-MDI	1168	759	0.16	0.54
$T = 75^\circ\text{C}$	Additive-free	583	427	0.06	0.36
	G-P400-MDI	2877	897	0.11	2.2
	G-P4000-MDI	1309	486	0.06	1.7
	G-P4000-MDI-HC	2063	1150	0.12	0.79
	G-P3000-MDI	1066	438	0.07	1.4
$T = 110^\circ\text{C}$	Additive-free	341	306	0.06	0.11
	G-P400-MDI	3516	977	0.07	2.6
	G-P4000-MDI	1105	750	0.06	0.47
	G-P4000-MDI-HC	1988	1081	0.06	0.84
	G-P3000-MDI	1166	868	0.07	0.34
$T = 150^\circ\text{C}$	Additive-free	–	–	–	–
	G-P400-MDI	3298	415	0.11	6.9
	G-P4000-MDI	740	519	0.06	0.43
	G-P4000-MDI-HC	1250	1082	0.06	0.16
	G-P3000-MDI	830	551	0.07	0.51



**Figure 3** Shear fracture sequence, during a stress-growth experiment, for a selected lubricating grease (G-P4000-MDI).

values, especially when relatively high shear rates are applied, also because fracture is a time-dependent phenomenon.<sup>24</sup> Nevertheless, the limiting non-steady stress values, corresponding to shear fracture visualization, are also provided in Tables III–VI. It is worth mentioning that, at low shear rate, the occurrence of shear fracture only appears after a long shearing time. However, the time necessary to reach the steady-state stress value, at low shear rate, can be even longer. Moreover, shear fracture is favored at high temperatures, and especially, in lubricating grease formulations including reactive polymer with high free NCO molar content (greases G-P400-MDI and G-P4000-MDI-HC).

From the analysis of the results shown in Tables III–VI, it can be deduced that the largest rheological modification was achieved by adding the polymer P400-MDI to the formulation. The effect that this additive exerts on the transient flow response of lubricating greases is clearly illustrated in Figure 1, where both additive-free and P400-MDI-based lubricating greases are compared. As can be observed, the rheological modification exerted by this polymer is especially significant during the first stages of the transient flow test, being the stress overshoot values much higher than those found for the additive-free lubricating grease. However, these differences are dampened as shear times increases (see, for instance,  $\tau_{\text{eq}}$  values), which indicates that the shear-induced structural breakdown in the P400-MDI-based lubricating grease is much more dramatic. The relative structural breakdown of these lubricating greases, during a transient flow test, has been quantified by means of the amount of overshoot,  $S^+$ , defined as follows:

$$S^+ = \frac{\tau_{\max} - \tau_{\text{eq}}}{\tau_{\text{eq}}} \quad (1)$$

$S^+$  values are shown in Tables III–VI for the lubricating greases studied, as a function of shear rate and temperature. As can be observed, in general, the P400-MDI-modified lubricating grease shows the highest  $S^+$  values, which points out that, as previously mentioned, this polymer induces an important rheological modification, especially related to the material viscoelastic response (transient flow curve up to the stress overshoot). In addition,  $t_{\max}$ , which is related to the beginning of the structural breakdown process, is generally larger for P400-MDI-based lubricating grease, excepting at 25°C, temperature at which the additive-free formulation shows extremely high values of  $t_{\max}$ .

The rheological modification achieved by adding the same amount of another polymer with higher molecular weight, i.e., P4000-MDI, is much less important (see Tables III–VI), being the effect generally more pronounced at high temperatures. As discussed in a previous work,<sup>8</sup> the addition of the same amount of these polymers to the lubricant implies a higher free NCO molar content in the P400-MDI-based lubricating grease. This fact corroborates the hypothesis<sup>6</sup> that the rheological modification of lubricating greases exerted by reactive polymers is predominantly due to the chemical reaction between these additives and the thickener agent, lithium 12-hydroxystearate in this study. Figure 2 compares the stress-growth curves of lubricating greases modified with P400-MDI and P4000-MDI, respectively, having the same molar free NCO content (0.163 mol NCO/kg grease). This identical NCO content was achieved, in the case of P4000-MDI-based lubricating grease, by increasing additive concentration (see Table II). As can be observed, the differences in the resulting rheological modification exerted by both polymers are now dampened, especially in the steady-state regime. However, it is worth remarking that the stress values, and the stress overshoot in particular, are generally higher for the lubricating grease formulation containing P400-MDI, in spite of its lower polymer concentration.

The influence of polymer functionality has been studied in greases containing P4000-MDI and P3000-MDI, with average functionality of 5.1 and 3.4, respectively, although in this case, the polymers have not so different number-average-molecular weights (see Table I). Both polymeric additives exert a similar rheological modification, although slightly higher values of  $\tau_{\max}$  and  $\tau_{\text{eq}}$  are usually observed, at low shear rates, for the formulation containing the branched polymer (Tables III–VI).

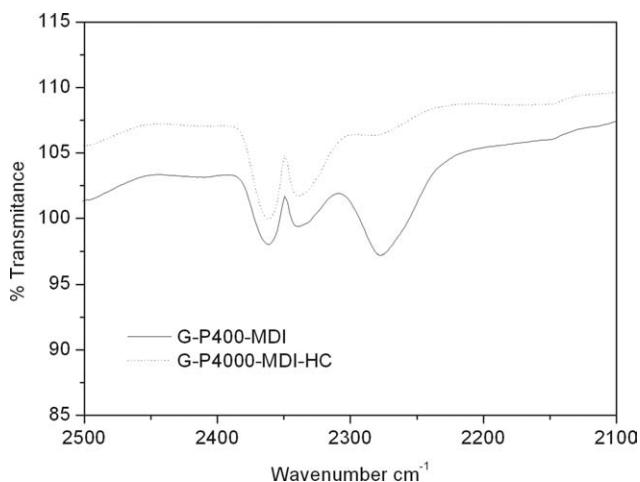
The influence of temperature on the transient flow response of the lubricating greases studied also depends on the polymeric additive employed. Thus, the values of  $\tau_{\max}$  and  $\tau_{\text{eq}}$  continuously decrease as temperature increases for the additive-free formula-

tion, as previously shown for other rheological parameters.<sup>27</sup> However, these characteristic parameters generally tend to increase with temperature, up to 75–110°C, when polymers P4000-MDI and P3000-MDI are included in the formulation, and then decrease at higher temperatures (Tables III–VI). However, the influence of temperature on the values of  $t_{\max}$  is usually the opposite. Aiming to explain this fact, it should be remarked that, apart from the standard thermal effects on grease rheology, at these high temperatures ( $\approx 150^\circ\text{C}$ ), the lubricating grease microstructural network, favored by the reaction between the lithium soap and the NCO-terminated polymers, may suffer some changes, due to the occurrence of undesirable chemical reactions. Thus, as was previously reported,<sup>7</sup> the carbamate groups can be partially reverted at high temperature, and then in absence of water, free isocyanate groups can react with urethane groups leading to allophanate or aryl-aryl urea derivatives reducing consequently the performance of these additives.

The influence of temperature on the transient flow response of P400-MDI-based lubricating grease is, once again, rather singular. In general, the values of  $\tau_{\max}$  and  $\tau_{\text{eq}}$  initially decrease with temperature, similarly to the response of the additive-free lubricating grease. However, both parameters start increasing at around 110°C. This rheological response should be attributed to the remaining free NCO groups in the lubricating grease after processing, which, at high temperature, are induced to react with either remaining free hydroxy groups of the metal soap or unreacted reactive polymer molecules. In this case, the P400-MDI-based lubricating grease, having the highest NCO content, is also the formulation with the highest amount of unreacted additive, as can be proved by IR spectroscopy. Figure 4 compares the FTIR spectra of greases G-P400-MDI and G-P4000-MDI-HC, initially with the same NCO total content, in a reduced wavelength window. As can be observed, the NCO absorption band, at 2277  $\text{cm}^{-1}$ , corresponding to the nonreacted polymer (or MDI in excess), is clearly more intense in the case of grease G-P400-MDI. On the contrary, this band is almost vanished for grease G-P4000-MDI-HC.

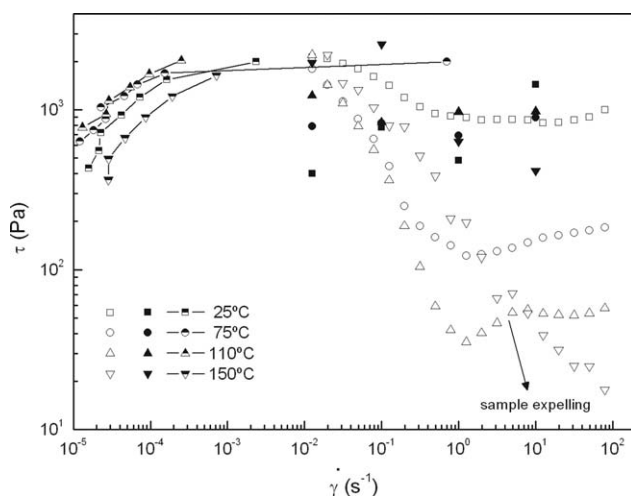
### Steady-state viscous flow behavior

Figures 5 and 6 show viscous flow curves for selected lubricating greases, obtained at several temperatures under different test conditions. Thus, step-shear rate and step-shear stresses ramps were applied using controlled-stress and controlled-strain rheometers, respectively. These flow curves have been also compared with the equilibrium (or pseudo-equilibrium) values obtained from stress-growth experiments. Traditionally, lubricating

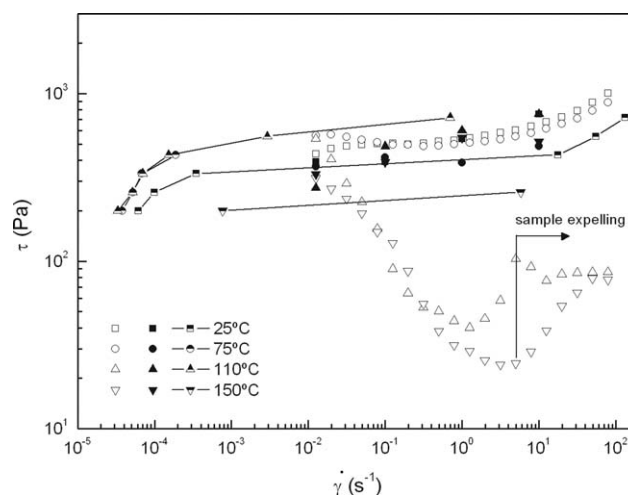


**Figure 4** IR spectra of selected lubricating greases (wavenumber window: 2100–2500  $\text{cm}^{-1}$ ).

greases have been considered yielding materials with extremely low values of the flow index, i.e. almost constant values of shear stress over decades of shear rate.<sup>28</sup> This yielding behavior is clearly noticed in the aforementioned figures. However, as was previously reported for a model additive-free lithium grease,<sup>27</sup> a minimum stress, at intermediate shear rates, is more apparent as temperature increases. This complex behavior is normally noticed at temperatures higher than 75°C, excepting for the P400-MDI-based formulation (see Fig. 5), which displays this minimum even at 25°C. A nonmonotonic flow model, in which three different steady flow regimes can be encountered by applying a constant shear stress, corresponding to three different values



**Figure 5** Shear stress versus shear rate curves, for G-P400-MDI grease sample, at different temperatures (filled symbols: equilibrium data from stress-growth experiments; open symbols: data from shear rate sweeps in a controlled-strain rheometer; half-filled symbols: data from shear stress sweeps in a controlled-stress rheometer).



**Figure 6** Shear stress versus shear rate curves, for G-P4000-MDI grease sample, at different temperatures (filled symbols: equilibrium data from stress-growth experiments; open symbols: data from shear rate sweeps in a controlled-strain rheometer; half-filled symbols: data from shear stress sweeps in a controlled-stress rheometer).

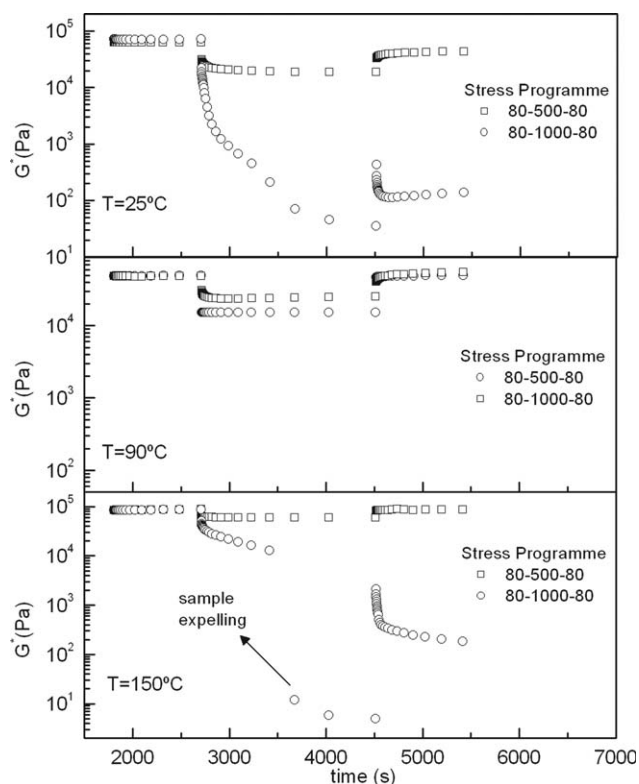
of shear rate, was previously proposed to explain this particular flow behavior.<sup>12,25</sup> In fact, only two possible steady flow regimes are possible since the other one corresponds to an unstable regime, which coincides with the part of the model in which the stress decreases with shear rate. Considering this model, a sudden transition from the low-shear rate regime to the high-shear rate regime was found in controlled-stress experiments, where the material behaves as a typical yield stress fluid. This flow behavior has been associated to a nonhomogeneous field of velocities during the viscometric flow of lubricating greases, as for instance, wall depletion and shear banding phenomena,<sup>20</sup> which can induce edge fracture. This fact is experimentally supported by the sequences shown in Figure 3. The use of the NMR velocity imaging technique has been also proposed to detect this nonhomogeneous flow regime.<sup>29</sup> As previously reported, edge fracture is related to changes in the rheological behavior with increasing shear rate as a consequence of secondary flows and instabilities.<sup>23,24</sup> In the case of the lubricating greases studied in this work, the fracture of the sample is clearly detected at high shear rates and, especially, at high temperatures, as previously discussed. According to this explanation, shear banding phenomena could be considered the origin of shear fracture. In fact, this nonmonotonic evolution of shear stress with shear rate was not so clearly observed when equilibrium (or pseudo-equilibrium) stress values obtained from stress-growth experiments were plotted versus the applied constant shear rates (Figs. 5 and 6). It should be remarked that pseudo-equilibrium stresses were obtained previously to the

detection of a significant fracture on samples submitted to a specific constant shear rate. Thus, for instance, some stress values plotted in Figure 5, at high temperatures and low shear rates, correspond to nonequilibrium data (see Tables III and IV).

On the other hand, in addition to the nonhomogeneous velocity field in the measuring gap previously discussed, the time effect needs to be considered, especially at low shear rates. In this sense, the time necessary to reach steady-state values is extremely long at the lowest shear rates studied, more than 2.5 hour in most cases. Therefore, shear time at a constant shear rate/stress, in a step-shear rate/stress ramp, is much shorter than that to reach steady-state values, at low shear rates, being of the order of  $t_{\max}$  in some cases. This means that the steady-state stress (or viscosity) value is generally overestimated in these tests, at least for shear rates lower than  $0.5 \text{ s}^{-1}$ . Unfortunately, a reliable steady-state value was not possible to be attained in some of these long tests, due to the occurrence of fracture.

### Rheo-destruction tests

In addition to the amount of overshoot previously defined, the shear-induced structural breakdown of lubricating greases, together with the subsequent structural recovery, may be studied by means of rheo-destruction tests.<sup>27</sup> These tests are based on the application of a sinusoidal stress inside the linear viscoelastic region, where the microstructure is almost unperturbed, and a subsequent stress outside the linear viscoelastic range, which may produce a certain degree of nonreversible structural breakdown. The recovery is then evaluated by applying, once again, a shear stress inside the linear viscoelastic region. Therefore, rheo-destruction tests simulate the behavior of lubricating greases during the starting up of a lubricated contact. Of course, the degree of irreversible structural breakdown depends, among other factors, on the magnitude of the stress value applied and measuring temperature. In this work, relatively gentle shear stresses (stress values around 55–60% beyond the critical stress for the onset of the nonlinear viscoelasticity regime) as well as larger stresses (1000 Pa) were applied on the samples studied, at three different temperatures. Figure 7 shows the evolution of the complex modulus during the application of these test protocols for a selected formulation. As can be expected, the complex modulus significantly decreases as the magnitude of the sinusoidal stress increases. However, when the stress inside the linear viscoelastic range is restored, a partial recovery is observed, depending on the polymeric additive included in the formulation. The percentage of rheo-destruction, relative to the values obtained in the linear viscoelastic range,



**Figure 7** Complex modulus decay, at different temperatures and a frequency of 1 Hz, after applying a shear stress outside the linear viscoelastic region, and further recovery when a shear stress inside the linear viscoelastic region is reimposed, for sample G-P400-MDI.

and the reversible structural breakdown can be obtained as follows:

$$\% \text{Rheo - destruction} = \frac{G_0^* - G_1^*}{G_0^*} \times 100 \quad (2)$$

$$\% \text{Recovery} = \frac{G_2^* - G_1^*}{G_0^* - G_1^*} \times 100 \quad (3)$$

being  $G_0^*$ ,  $G_1^*$ , and  $G_2^*$  the values of the complex modulus in the linear viscoelastic region after the application of a stress value outside the linear viscoelastic range, and after restoring the initial stress value, respectively.

The rheo-destruction and recovery values obtained are listed in Table VII, as a function of temperature, for the different formulations studied. As previously reported,<sup>27</sup> the percentage of rheo-destruction increases with both the magnitude of the stress applied and temperature for the additive-free lubricating grease. On the contrary, the percentage of recovery usually decreases by increasing the stress and temperature, excepting after applying a high stress value where the recovery is very similar independently on the temperature applied.

However, this behavior is much more complex in the case of lubricating greases containing NCO-terminated polymers, especially when the effect of



**TABLE VII**  
**Rheo-Destruction and Recovery Percentages for the Lubricating Greases Studied**  
**After the Application of Different Shear Stresses Outside the Linear Viscoelasticity**  
**Region as a Function of Temperature**

	Stress program (Pa)	Temperature (°C)	Rheo-destruction (%)	Recovery (%)
Additive-free grease	10-200-10	25	32.60	20.55
		90	48.60	84.40
		150	99.20	49.20
	10-1000-10	25	99.50	49.20
		90	99.90	48.30
		150	99.90	52.00
G-P400-MDI	80-500-80	25	67.95	51.16
		90	31.48	97.83
		150	27.52	100
	80-1000-80	25	99.95	0.12
		90	49.91 <sup>a</sup>	85.45 <sup>a</sup>
		150		
G-P4000-MDI	30-250-30	25	93.02	20.78
		90	5.92	65.64
		150	99.68	24.79
	30-1000-30	25	99.82	57.54
		90	99.98	39.84
		150	99.97	6.63
G-P4000-MDI -HC	100-250-100	25	37.19	47.43
		90	31.85	69.37
		150	70.53	39.53
	100-1000-100	25	98.52	35.10
		90	99.92	28.44 <sup>a</sup>
		150		
G-P3000-MDI	10-250-10	25	85.80	65.83
		90	66.60	65.85
		150	99.60	28.03
	10-1000-10	25	99.60	49.46
		90	100	22.06
		150	100	20.65

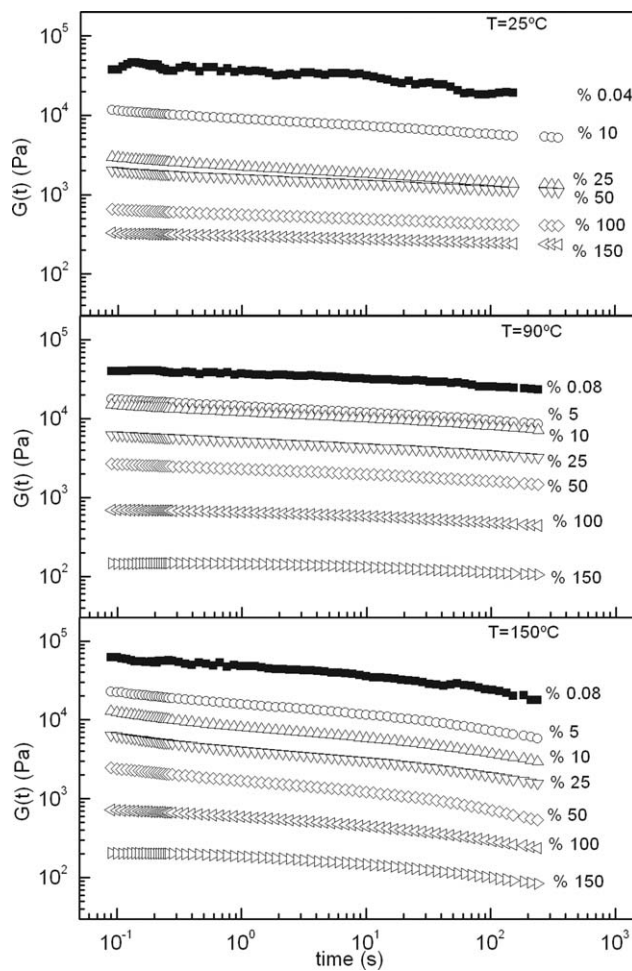
<sup>a</sup> Fracture and sample expelling from the gap.

temperature is considered. In general, these formulations exhibit higher values of rheo-destruction than those found in the additive-free lubricating greases when a moderate stress value outside the linear viscoelastic range is applied, excepting at 90°C where much lower rheo-destruction values than expected were found. Similarly, the recovery values were generally lower than those obtained for the polymer-free lubricating grease, excepting, once again, at 90°C. As previously mentioned, this apparent structural reinforcement at moderate temperatures can be explained by considering the number of free NCO groups in the formulation able to react at these temperatures. At higher temperatures (150°C), the usual thermal effect on grease microstructure is predominant. Once again, the P400-MDI-based lubricating grease shows a particular behavior, with generally improved structural resistance than the others samples, especially at high temperatures. Thus, a lower rheo-destruction, and higher recovery, is favored at high temperatures, i.e., 27.5% rheo-destruction at 500 Pa and 150°C, probably due to the

higher amount of unreacted NCO groups, as previously discussed.

### Stress relaxation tests

Figure 8 shows the evolution of the relaxation modulus with the elapsed time since sample deformation occurred, at different constant applied strains, inside and outside the linear viscoelasticity region, for a selected lubricating grease formulation studied. It is well-known that the nonlinear relaxation modulus is strain dependent,  $G(\gamma, t)$ , as a consequence of the strain-induced structural modification. Therefore, a subsequent decrease in  $G(\gamma, t)$  is noticed by applying increasing strain values beyond the critical value which delimits the linear viscoelastic range (around 0.1% in Fig. 8). Moreover, as can be seen in the same figure, the relaxation modulus follows a power-law decay with the elapsed time, displaying very similar slope values independently of the shear strain applied on the sample. Consequently, the time-strain



**Figure 8** Linear and nonlinear relaxation modulus versus elapsed time for a selected lubricating grease, G-P400-MDI, at different temperatures.

separability for the nonlinear viscoelasticity function can then be assumed:

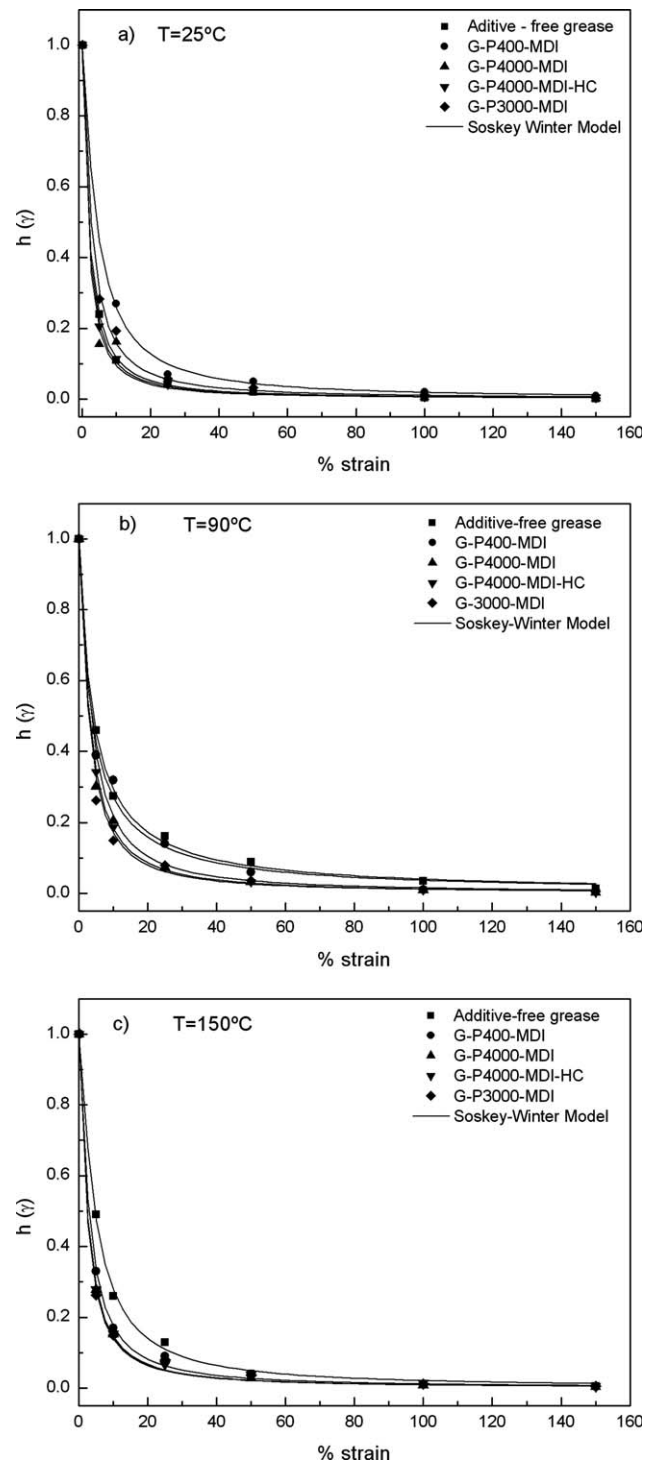
$$G(\gamma, t) = G(t) \cdot h(\gamma) \quad (4)$$

where  $G(t)$  is the linear relaxation modulus and  $h(\gamma)$  is the so-called “damping function” which takes into account the nonlinear effects. Assuming this factorization, the evolution of the transient stress and steady-state flow curves of lubricating greases can be predicted in terms of a factorable nonlinear constitutive equation, as previously reported.<sup>30</sup>

The damping function is a rheological parameter that can be used to evaluate the structural resistance of greases under shear, although, in this case, at constant applied strain. Figure 9 shows the values of the damping function calculated from eq. (4), for the lubricating greases studied and different temperatures. As can be observed, the values and the evolution of the damping function are quite similar for all the greases studied. In this sense, a dramatic decrease in the values of this function is always noticed, even

at relatively low values of the applied strain. The Soskey-Winter (1984) model<sup>31</sup> fits the shear strain dependence of the damping function ( $R^2 > 0.993$ ):

$$h(\gamma) = \frac{1}{1 + a\gamma^b} \quad (5)$$



**Figure 9** Evolution of the damping function with shear strain, at different temperatures, for the lubricating greases studied.

TABLE VIII  
Values of the Soskey-Winter Parameter *a* for  
the Lubricating Greases Studied as a  
Function of Temperature

	Temperature (°C)	<i>a</i>
Additive-free grease	25	0.43
	90	0.14
	150	0.15
G-P400-MDI	25	0.16
	90	0.16
	150	0.27
G-P4000-MDI	25	0.54
	90	0.27
	150	0.34
G-P4000-MDI-HC	25	0.49
	90	0.25
	150	0.33
G-P3000-MDI	25	0.30
	90	0.20
	150	0.35

where “*a*” and “*b*” are material parameters. The values found for parameter “*b*” are  $1.25 \pm 0.20$  in all cases, and consequently, this parameter may be fixed for the sake of simplicity ( $R^2 > 0.990$ ). The values of parameter “*a*” are collected in Table VIII for the different formulations and temperatures studied. As can be observed for the additive-free lubricating grease, the value of parameter “*a*” is higher at 25°C, and then decreases at 90 and 150°C, which means that the microstructure of this grease is more strongly affected by the deformation at low temperature. Thus, the linear relaxation modulus shows the highest values at 25°C, however its microstructure is more easily destroyed by applying a deformation outside the linear viscoelastic region. Likewise, the influence of temperature on the damping function is different for greases containing NCO-terminated polymers. In general, polymer-based formulations show higher values of “*a*,” which generally shows minimum values at 90°C. Taking into account that  $G(t)$  is not largely affected by temperature, these experimental results seem to indicate that grease microstructure at 90°C is more shear resistant, which supports the discussion sustained in previous sections. Finally, P400-MDI-based lubricating grease shows much lower values of parameter “*a*” than those found for other polymer-based formulations, especially at 25 and 90°C. In this case, an apparent slightly lower resistance to deformation was found at 150°C, although this result is also associated to higher values of  $G(t)$  at this temperature.

## CONCLUSIONS

NCO-terminated polymers, used as reactive additives in lithium 12-hydroxystearate lubricating grease formulations, significantly modify grease rheological

behavior. The largest rheological modification was achieved by adding the lowest molecular weight polymer to the additive-free lubricating grease, fact that has been related to its higher free NCO content and larger mobility, being this effect more pronounced at high temperatures. In general, NCO-terminated polymers significantly dampen the influence of temperature on the rheological functions of the additive-free lubricating grease. However, in some cases, the viscous and viscoelastic functions analyzed increase with temperature, especially in formulations with residual free NCO groups, which may be induced to react at high temperatures. The modification exerted by these polymers on the transient flow response is particularly important during the first stages of the stress-growth curve, being the values of the stress overshoot much higher than those found for the additive-free lubricating grease. Several experimental flow problems such as fracture and sample expelling from the measuring tool have been usually found. These problems were enhanced in formulations including NCO-terminated polymers, especially those including polymers with low molecular weights.

In general, formulations including NCO-terminated polymers exhibit higher values of rheo-destruction than those found in additive-free lubricating greases, excepting at 90°C where much lower rheo-destruction values than expected were found. Similarly, the recovery values were generally lower than those obtained for the polymer-free lubricating grease, excepting once again at 90°C. Identically, the damping function takes maximum values at around 90°C, indicating that grease microstructure at 90°C is more resistant to shear deformation.

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