Greases additised with phosphonium-based ionic liquids - Part I: rheology, lubricant film thickness and Stribeck curves

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Abstract

Two greases formulated with lithium complex and anhydrous calcium thickeners were mixed with cation phosphonium-derived ionic liquids with the aim of studying their rheology, lubricant film forming properties, and the friction behavior under different temperatures and speeds. The addition of the ionic liquids decreased viscosity, yield stress, storage modulus and loss modulus of the greases, with larger effect on anhydrous calcium-based grease. The viscosity reduction led to lower friction results under both temperatures and range of speeds tested. The trihexyltetradecylphosphonium decanoate ionic liquid had the higher influence on the above-mentioned properties, especially mixed with the anhydrous calcium-based grease.

Keywords: phosphonium ionic liquids; additive; greases; rheology; lubricant film thickness; friction.

1. Introduction

Originally, the lubricating greases consisted of a blend of olive oil and lime or even animal fat that were usually used to lubricate the bearings of the carriages. These substances were used until the 19th century, when the first greases based on mineral oil began to be developed, after oil was discovered in the USA in 1859. The first patents for complex calcium and lithium greases appeared, in the middle of the 20th century and soon after, other types of greases emerged [1,2]. About 10-15 % of the fats are formed by the thickener, which is used for their classification. The rest of the compound is oil, that can be mineral or synthetic, and liquid or solid additives [3]. Many different additives have been introduced over the years [4,5], in particular anti-wear additives, used to improve the tribological behaviour of lubricating greases. but more recently many authors have been focusing their attention on ionic liquids (ILs) [5–8].

These salts (ILs) are formed by a combination of organic and inorganic ions (cations and anions) that in general are liquid at room temperature [9]. They have several properties that make them good candidates for use in lubrication [9–12]. For instance, the possibility of selecting the physical-chemical properties of these compounds by combining anions and cations is a good option to obtain particular ILs for a specific activity [13–15]. The earlier studies on the use of ILs as lubricants evaluated the behaviour of imidazolium cations combined with tetrafluoroborate (BF_4) and hexafluorophosphate (PF_6) anions [16]. The imidazolium cation was also investigated in combination with many other anions formed by different length alkyl chains or different functional groups [14,17–20]. Qu *et al.* synthesized a group of new alkylammonium ILs and studied their lubricating properties on aluminium surfaces and important friction and wear reductions were found [21,22].

Most studies used ILs as additives in very small concentrations due to their low miscibility in non-polar hydrocarbon oils [20,23–26]. However, Yu *et al.* found good miscibility of two phosphonium-based ILs in mineral and synthetic oils [27]. Qu *et al.* also studied the IL trihexyltetradecylphosphonium bis(2-ethylhexyl) phosphate as a lubricant additive, which showed good miscibility in various hydrocarbon oils, good thermal stability, no signs of corrosion, good wettability on solid surfaces and very good antiwear properties [28]. Battez *et al.* have studied the physical-chemical properties and tribological behaviour of several phosphonium-based ILs both neat and as additives in different oils [29–34]. Most of these ILs were non-corrosive and miscible in mineral or synthetic oils. They also showed good antifriction and antiwear results even compared to ZDDP (zinc dialkyldithiophosphate), which is a typical additive with very good tribological properties used in the formulation of lubricating oils.

Concerning greases, Liu *et al.* studied the tribological performance of five imidazolium ILs used as additives (1 wt.%) in a polyurea grease in steel/steel contacts [5]. The results were compared with those of the base grease also additised at 1 wt.% with ZDDP. Friction and wear reductions were reached with the IL-grease blends at high temperatures compared to the base grease and the ZDDP-additised grease. In 2011 [6], imidazolium-based ILs containing benzotriazole were synthesized and used as antiwear and anticorrosion additives in a poly(ethylene glycol) (PEG) grease and a polyurea grease. The tribological tests performed in steel/steel contacts at room temperature and 150 ºC demonstrated the effectiveness of these ILs as antifriction and antiwear additives. The tribological characteristics of the IL-grease blends were better than those of the ZDDP-containing grease.

Wang *et al.* synthesized three phosphonium-based ILs and studied the tribological behavior of a grease formulated with a polyalphaolefin (PAO 10) as base oil, lithium as thickener and the ILs as additives [7]. Regarding the rheological behavior, the addition of the ionic liquid caused a decrease in both the storage modulus (G') and the loss modulus (G"), but the ILs improved the reduction of friction and anti-wear properties of the base grease. Recently, Ploss *et al*. [8] studied the tribological behavior of four halogen-free phosphonium-based ILs as additives of two greases that used polypropylene and lithium-complex as thickener. Friction and wear reductions were obtained with the additivation with some of these ILs.

The aim of this work is to evaluate the possibility of replacing the traditional antifriction/antiwear additives, used in the formulation of greases, by ILs. For that purpose, two grease were proposed, containing the same mineral base oil but different thickeners: lithium complex and anhydrous calcium. Each grease was separately additised with three different phosphonium-based ILs, in two different percentages (2 and 5 wt.%), resulting in fourteen different fully formulated products.

The rheological characterization of the greases consisted of rotational tests at low shear rate to determine the yield stress and of oscillatory tests to evaluate the storage and loss moduli, respectively G' and G''. The tribological behaviour of the greases included lubricant film thickness measurements in an elliptical contact at different temperatures and speeds, and Stribeck curves at different temperatures.

2. Methodology

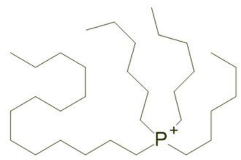
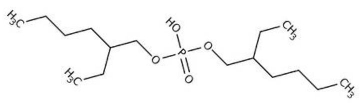
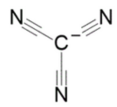
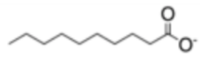
2.1. Greases and ionic liquids

A lithium-based grease and an anhydrous calcium-based grease were used in this work. These greases were provided by Axel Christiernsson International company (Sweden) and their main properties are shown in Table 1. On the other hand, the ILs used as additives were provided by IOLITEC GmbH (Germany). The tested ILs are synthetized with the same cation trihexyltetradecylphosphonium [$P_{6,6,6,14}$] but different anions: bis(2-ethylhexyl)phosphate [BEHP], decanoate [DEC], and tricyanomethanide [TCM], and their chemical descriptions can be found in Table 2. The mixtures of the non-additised greases and the ILs used as additives at 2 and 5 wt.% were prepared in a planetary centrifugal mixer (Kakuhunter SK-300 SII) at 1600 rpm in two 5 min cycles and a final degassing step of 2 min at 2200 rpm.

Table 1. Properties of the greases.

Designation	Thickener (wt.%)	Base oil	Base oil viscosity ($mm^2 \cdot s^{-1}$) 40 ºC	Base oil viscosity ($mm^2 \cdot s^{-1}$) 100 ºC	Worked penetration (1/10 mm) 60 strokes	NLGI grade
G1	Lithium complex (8.6)	Mineral oil	200	14.6	270	2
G2	Anhydrous calcium (7.6)	Mineral oil	176	13.6	277	2

Table 2. Chemical description of the ionic liquids.

Designation		IL1	IL2	IL3
IUPAC Name		Trihexyltetradecyl phosphonium bis(2-ethylhexyl)phosphate $[P_{6,6,6,14}][BEHP]$	Trihexyltetradecyl phosphonium tricyanomethanide $[P_{6,6,6,14}][TCM]$	Trihexyltetradecyl phosphonium decanoate $[P_{6,6,6,14}][DEC]$
Empirical formula		$C_{48}H_{102}O_4P_2$	$C_{36}H_{68}N_3P$	$C_{42}H_{87}PO_2$
Chemical Structure	Cation			
	Anion			

2.2. Rheology tests

The rheological behavior of the greases was analyzed through rotational and oscillatory tests. The rotatory tests were performed at 25 and 80 ºC, using a HAAKE RS50 rheometer with a serrated plate-plate geometry (ϕ = 35 mm) and a 0.5 mm gap. Before performing these tests, the grease samples were subjected to a pre-shear procedure in order to reduce the differences between samples due to their previous history, internal stresses and handling, and thus improving the reproducibility of the rheological tests. The pre-shear procedure (similar to the one reported by Gonçalves et al. [35]) was performed as described in Table 3.

Table 3. Description of the pre-shear procedure.

Step	Actions
1	The grease is applied on the bottom plate, without spreading.
2	The upper plate is lowered to the pre-defined gap.
3	The excess of grease is trimmed, and the sample remained for 10 min at the test temperature.
4	The sample is then subjected to an oscillatory motion for 1 min under an angular frequency of 1 Hz and subjected to a constant strain of 0.1%.
5	A final rest (no stress) period of 3 min is applied, at constant temperature.

The rotational test consisted in a stress sweep from 0.6 to 1000 Pa during 10 min, obtaining a typical flow curve. The shear rate was also measured, and the yield stress was determined from the experimental data.

The oscillatory test was performed using a HAAKE RHEOSTRESS 1 rheometer with a 20 mm-diameter plate-plate configuration. The same pre-shear procedure (Table 3), was performed before each test. Finally, the test consisted of an oscillatory movement at the frequency of 1 Hz and a stress sweep from 1 to 2000 Pa. The storage module, G' (representing the elastic character of the grease) and the loss module, G'' (representing the viscous character of the grease) were measured as a function of the shear stress at 25 and 80 ºC.

2.3. Tribological testing

The lubricant film thickness was measured for all lubricant samples (non-additised greases and their mixtures with the ILs) in an EHD2 rig. This tribometer (PCS Instruments Ltd., U.K.) is capable of measuring the central film thickness in the lubricated contact of a ball against a flat disc, under variable speed, temperature, slide-to-roll ratio (SRR) and load. The interferometry method is used by the EHD2 rig to measure the central film thickness, as described in [36].

Before the tests, the specimens (disc and ball) were cleaned with petroleum ether and then air-dried. The thickness of the glass disc space layer was measured statically, without grease, pressing the ball against the disc with a load of 50 N, the procedure is necessary in order to obtain an accurate evaluation of the lubricant film thickness [37]. A grease scoop was used for ensuring the fully flooded condition, forcing the grease back into the track. Table 4 shows the test conditions used in the lubricant film thickness measurements. At the beginning of each new test, the grease samples were heated for 10 min when the tests were performed at 40 ºC, and for 20 min if the test temperature was 80 or 120 ºC. A new grease sample was added before each test at different temperature and the same grease volume was used in each test.

Table 4. Operating conditions for measuring the film thickness in the EHD2 test rig.

	Steel ball	**Disc**
Radius – $R_{x,y}$ (mm)	9.525	–
Roughness – *Ra* (nm)	≤ 20	~ 5
Materials	AISI 52100	Glass
Elastic modulus – *E* (GPa)	207	64
Poisson coefficient – ν	0.29	0.20
Load – *L* (N)	50	
Maximum contact pressure – p_o (GPa)	~ 0.7	
Temperature – *T* (ºC)	40, 80, 120	
Entrainment speed – *Uo* (mm/s)	10 – 2000	
Slide-to-roll ratio – *SRR* (%)	5	

A Mini Traction Machine MTM-2 (PCS Instruments Ltd., U.K.) test rig was used to measure the traction in a ball-on-disc contact and obtain the so-called Stribeck curve of the grease samples (non-additised and blended with ILs).

The MTM test parameters are shown in Table 5. The specimens were cleaned using the same procedure described before for the film thickness tests. Traction was measured during the tests and the grease sample and the specimens were not changed between tests at the two temperatures. The temperature of the tests performed in the EHD2 and MTM-2 refer to the pot temperature, therefore the temperature in the vicinity of the contact might be slightly different. The Stribeck curves were determined at a fixed SRR of 5% and variable entrainment speed ranging from 20 to 900 mm/s. The sliding speed was calculated by using the Eq. (1), where u_{ball} and u_{disc} are the tangential speed of the ball and the disc at the point of contact, respectively. On the other hand, the SRR was calculated by using the Eq. (2), being $|u_{disc} - u_{ball}|$ the sliding speed.

$$Vs = u_{disc} - u_{ball} \tag{1}$$

$$SRR = 2 \cdot \frac{|(u_{disc} - u_{ball})|}{(u_{disc} + u_{ball})} \times 100\% \tag{2}$$

Table 5. Experimental details for the MTM tests.

Parameters	Ball	Disc
Radius – $R_{x,y}$ (mm)	9.525	–
Roughness – Ra (nm)	< 20	< 20
Materials	AISI 52100 (steel)	
Young's modulus – E (GPa)	207	207
Poisson coefficient – ν	0.29	0.29
Load – L (N)	50	
Maximum contact pressure – p_o (GPa)	1.11	
Temperature – T (ºC)	80, 120	

3. Results and discussion

3.1. Rheology

3.1.1. Rotational tests

Figure 1 shows the shear stress as a function of the shear rate. The shear rate axis scale is set to logarithmic, so that the low shear rate region can be observed. Both lithium complex and anhydrous calcium-based greases hardly change their rheological behavior with the addition of IL2 at the two temperatures. However, the viscosity of the blend of G2 + 2 wt.% of IL2 decreases at 25 ºC due to lower shear stress values under identical shear rate values. On the other hand, the viscosity of the blends of both greases separately mixed with IL1 and IL3 also decreased in comparison with the viscosity of the base greases because of the lower shear stress values.

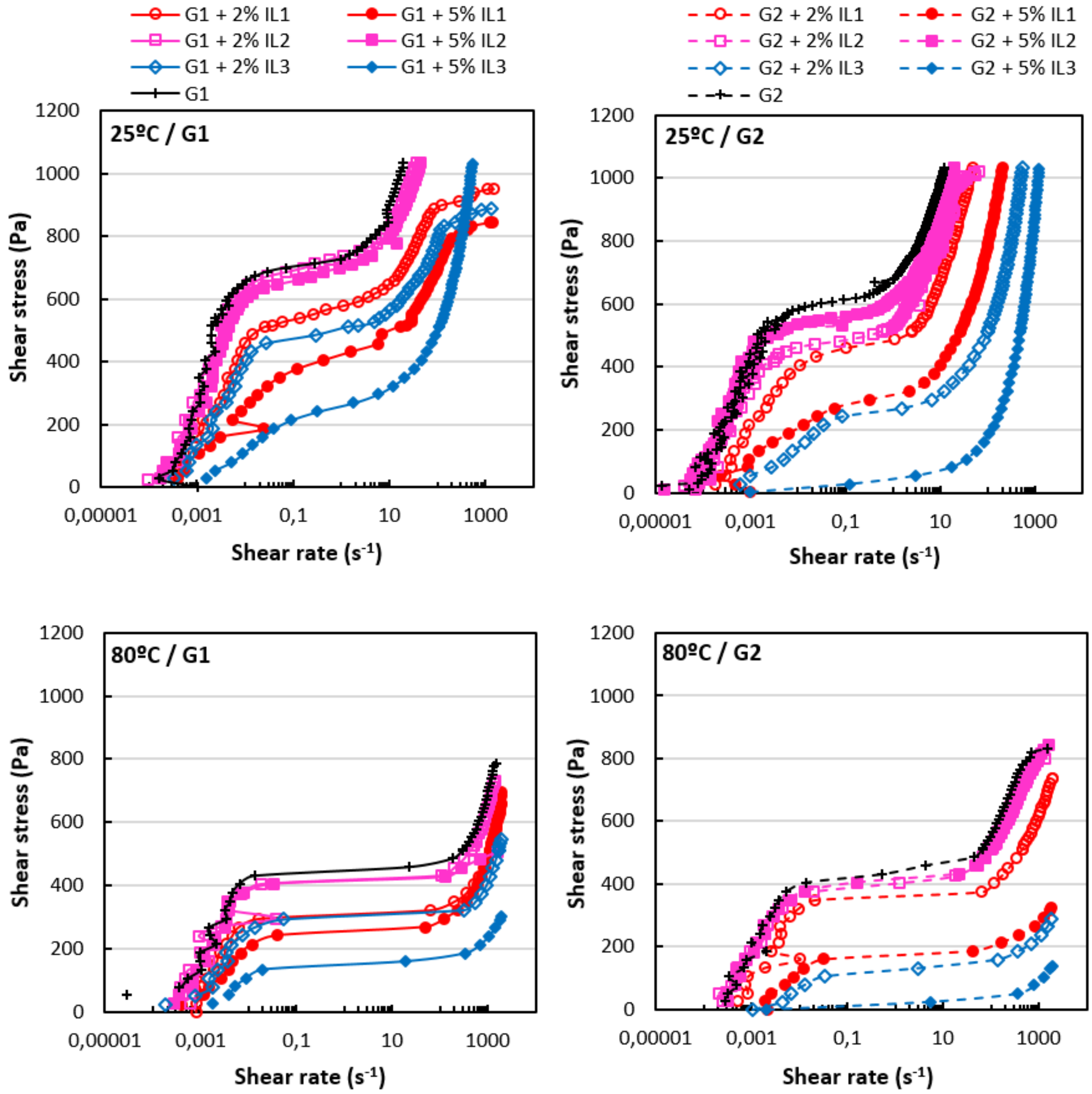


Figure 1: Flow curves of greases G1 (left) and G2 (right) at 25 and 80 ºC.

The yield stress (τ_y) of each grease sample is presented in Figure 2. It was determined using the procedure developed by Couronne et al. [38].

This stress value indicates the point at which the grease starts to flow. However, it has been reported that grease may flow before this stress value is reached [39, 40]. The physical interpretation of yield stress is difficult because, among other things, there is no consensus on how to measure it.

With the addition of the ILs the greases become more fluid and hence their yield stress decreases. However, in the case of the G1 + IL2 blend, the yield stress hardly changed at both temperatures, in comparison with the other blends. Similar results were obtained for the G2 + IL2 blend at 80 ºC. On the other hand, the IL3-containing samples showed the lowest yield stress (τ_y) values.

In general, the higher are the IL content and temperature, the lower is the yield stress [41].

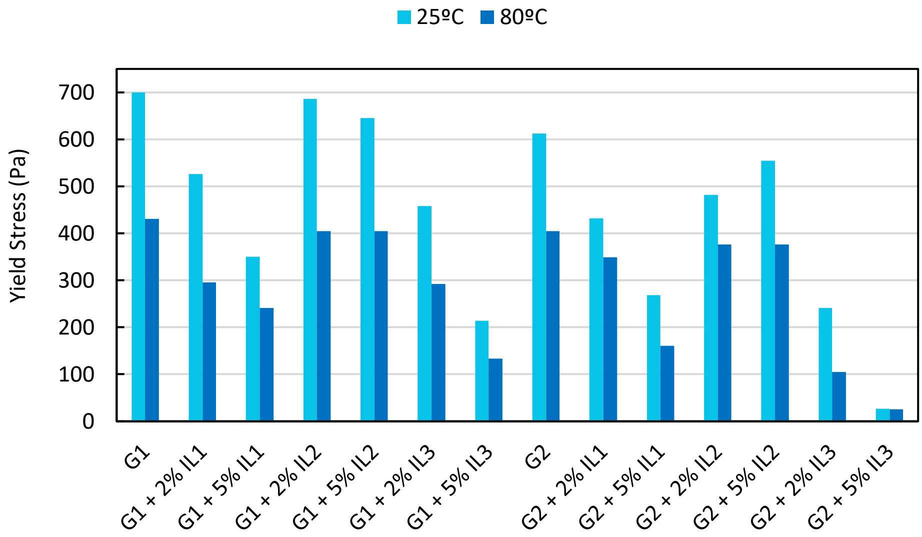


Figure 2. Yield stress of greases G1 and G2, at 25 and 80 ºC.

3.1.2. Oscillatory tests

Figures 3 and 4 show the storage modulus (G') and the loss modulus (G'') of the base greases and their mixtures with the ILs at the two test temperatures (25 and 80 ºC), plotted against the shear stress. The addition of IL1 and IL3 decreased both the G' and G'', which is emphasized when the IL concentration is higher. This effect of the ILs in the elastic and viscous behaviors of the greases is especially remarkable for IL3. On the other hand, the blends with IL2 showed a very similar behavior to those of their base greases. This influence of IL2 was similar to that in the rotatory tests.

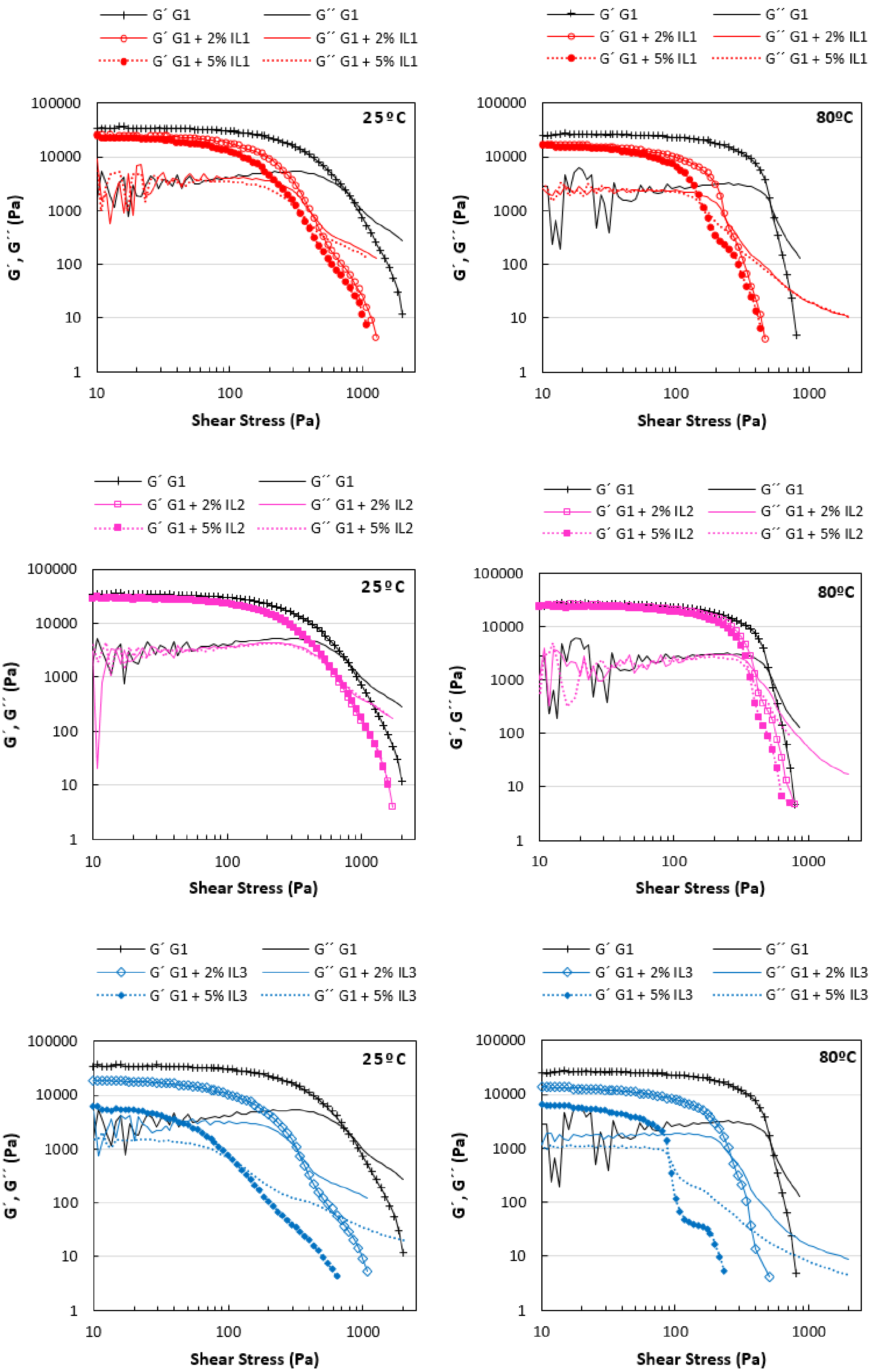


Figure 3. G' and G" modulus of grease G1 blended with the ILs at 25 and 80 ºC.

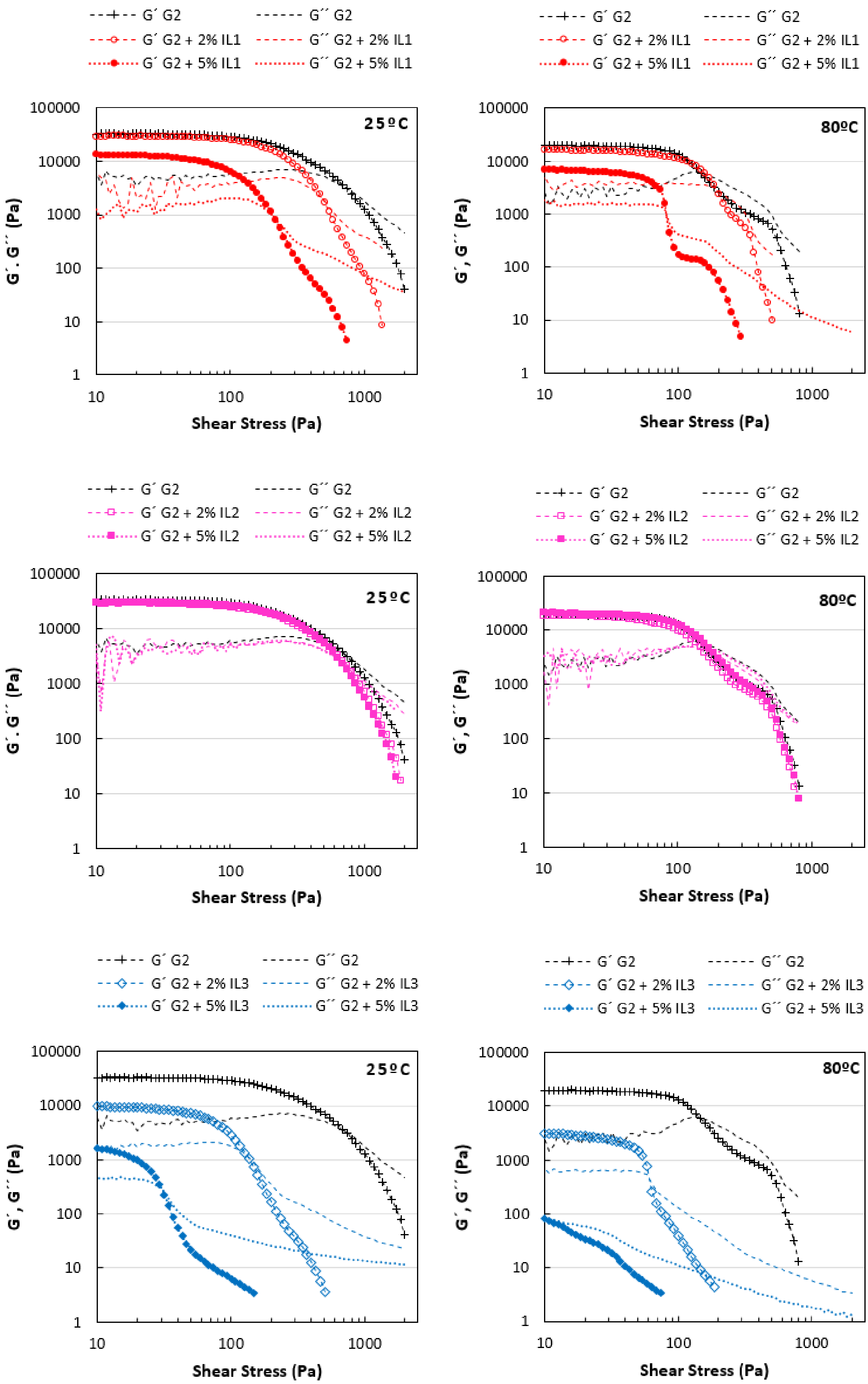


Figure 4. G' and G" modulus of grease G2 blended with the ILs at 25 and 80 ºC.

Table 6 presents the shear stress values at which G' and G" have the same value and hence tanδ =1. From these shear stress values onwards, the loss modulus (G") becomes higher than the storage modulus (G'), indicating that the grease starts flowing [40]. In general, the addition of the ILs reduced the values of shear stress for tanδ =1 of both base greases. Those values are higher for the lithium-based greases than those of their calcium-based counterparts. The increase of the IL concentration decreased the shear stress at which G' = G" (tanδ =1).

Table 6. Shear stress values for G' = G" (tanδ =1).

Grease sample	**Shear stress (Pa)**	
	25 ºC	80 ºC
G1	796.0	542.2
G1 + 2% IL1	430.7	251.6
G1 + 5% IL1	369.4	158.7
G1 + 2% IL2	632.2	398.9
G1 + 5% IL2	682.7	369.4
G1 + 2% IL3	342.1	271.7
G1 + 5% IL3	116.8	92.7
G2	737.2	147.0
G2 + 2% IL1	502.2	199.9
G2 + 5% IL1	233.0	85.9
G2 + 2% IL2	737.2	158.7
G2 + 5% IL2	682.7	171.4
G2 + 2% IL3	136.1	63.2
G2 + 5% IL3	31.7	10.8

3.2. Tribological testing

3.2.1 Lubricant film thickness

Figure 5 shows the lubricant film thickness as a function of speed for each lubricant sample under the three test temperatures (40, 80 and 120 ºC). The represented values are the average of two tests of each lubricant sample. As expected, the film thickness shows a linear increase (on a logarithmic scale) with increase of the entrainment speed under all temperatures. The reported behavior is similar to that found for base oils due to the hydrodynamic effect promoted by increasing speed [42]. In addition, it can be observed an increase of the lubricant film thickness at both higher temperature and low speeds. This phenomenon is attributed to the fact that, under these conditions, the thickener is more prone to cross the contact, increasing the lubricant film thickness which contributes to the surface separation and to support the load [36,42–46].

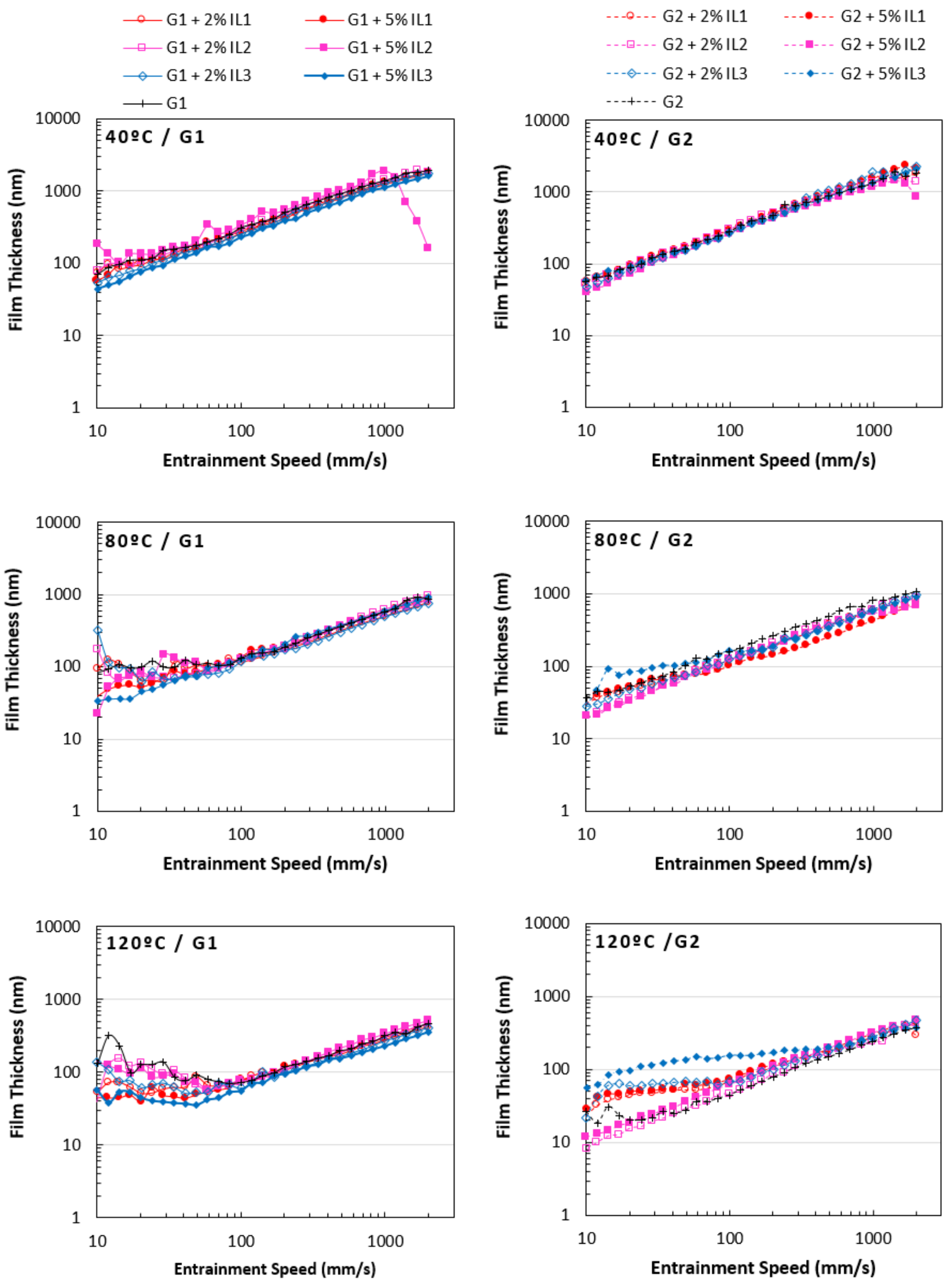


Figure 5. Lubricant film thickness of the base grease and their blends with the ILs.

The blends of the lithium complex-based grease (G1) with the IL1 show very similar lubricant film thickness results to those of the base grease at the lowest temperature (40 ºC), Table 7. Meanwhile, the blends with the IL2 at higher concentration (5 wt.%) show a significantly higher lubricant film thickness than the base grease. For blends with the IL3, the lubricant film thickness decreases when the IL concentration is higher. The blends of the anhydrous calcium-based grease with both IL1 and IL3 (for both concentrations) show similar lubricant film thickness values to those of the base grease. However, the anhydrous calcium-based grease blended with IL2 at the highest concentration (5 wt.%) shows a slightly reduced lubricant film thickness when compared to the base grease.

At 80 °C, the lubricant film thickness for the blends of the lithium complex-based grease with the three ILs decreases in comparison to that of the base grease at lower speeds and all lubricant samples behave similarly to the base grease as test speed increases. The lubricant film thickness for the blends with IL1 and the neat anhydrous calcium-based grease is very similar at low speeds (50 mm/s) and slightly different at higher speed (500 mm/s), Table 7. For blends with IL2, the lubricant film thickness decreases when compared to the base grease, independently of speed. On the other hand, the blends with the higher concentration of IL3 show increased film thickness at low speeds, but as the speed increases the lubricant film thickness decreases to less than that of the base grease for both IL concentrations.

At the highest test temperature (120 °C), all the mixtures of IL with the lithium complex-based grease show film thicknesses values lower than the base grease at low speeds and similar values as the speed increases. With the anhydrous calcium-based grease (G2), the blends with IL1 show slightly higher film thickness values than the base grease for all concentrations, however the differences are negligible at high speeds (>1000 mm/s). At low speeds, the G2 + IL2 blend show slightly higher lubricant film thickness values than the base grease. On the other hand, the lubricant film thickness increases considerably at low speeds for the G2 + IL3 blend. The lubricant film thickness of all samples leads to similar values, at high speeds.

Table 7. Lubricant film thickness (nm) at entrainment speeds of 50 and 500 mm/s.

Grease sample	**50 mm/s**			**500 mm/s**		
	40 ºC	80 ºC	120 ºC	40 ºC	80 ºC	120 ºC
G1	176	108	90	915	359	197
G1 + 2% IL1	160	106	85	800	316	174
G1 + 5% IL1	163	83	48	829	361	190
G1 + 2% IL2	182	80	66	909	371	182
G1 + 5% IL2	205	114	72	1022	356	215
G1 + 2% IL3	152	77	52	813	304	162
G1 + 5% IL3	138	74	35	706	371	153
G2	159	100	27	888	492	148
G2 + 2% IL1	166	74	53	886	367	187
G2 + 5% IL1	173	75	61	951	255	179
G2 + 2% IL2	169	73	29	901	384	163
G2 + 5% IL2	150	69	36	785	361	195
G2 + 2% IL3	157	74	68	1038	358	175
G2 + 5% IL3	157	108	136	864	337	200

3.2.2 Coefficient of friction (COF)

Figure 6 shows the Stribeck curves (COF versus entrainment speed in this case) of both greases and their blends with the ILs. It can be observed that the rise in temperature reduced friction in all cases, which is due to the decrease of viscosity. The addition of IL1 to both greases reduced their viscosity, as reported in Fig. 1, but the friction behavior of each grease and their mixtures was dependent on the temperature, on the speed and on the thickener type. In general, the IL-containing blends showed stable friction behavior at both temperature and the range of speed tested. Only the G2 + 5%IL1 blend showed remarkably lower friction coefficient at decreasing speed in the test performed at 80 ºC.

The friction behavior of the blends containing the IL2 was very similar to the case with the IL1. The use of these blends also led to a stable friction coefficient, irrespective of the speed range and temperature values tested. The neat lithium-based grease showed again a rising friction behavior from a speed of 100 mm/s onwards.

The tests performed with the samples additised with IL3 show a coefficient of friction which is very dependable on the speed range, temperature and grease type. In this case, only the IL3-containing blends at 2 wt.% showed a stable coefficient of friction along the whole speed range, with the exception of the blend with G1 at 120 ºC, where friction increased from 100 mm/s backwards. Meanwhile, the blends containing 5 wt.% of IL3 show less variation with speed at the higher temperature.

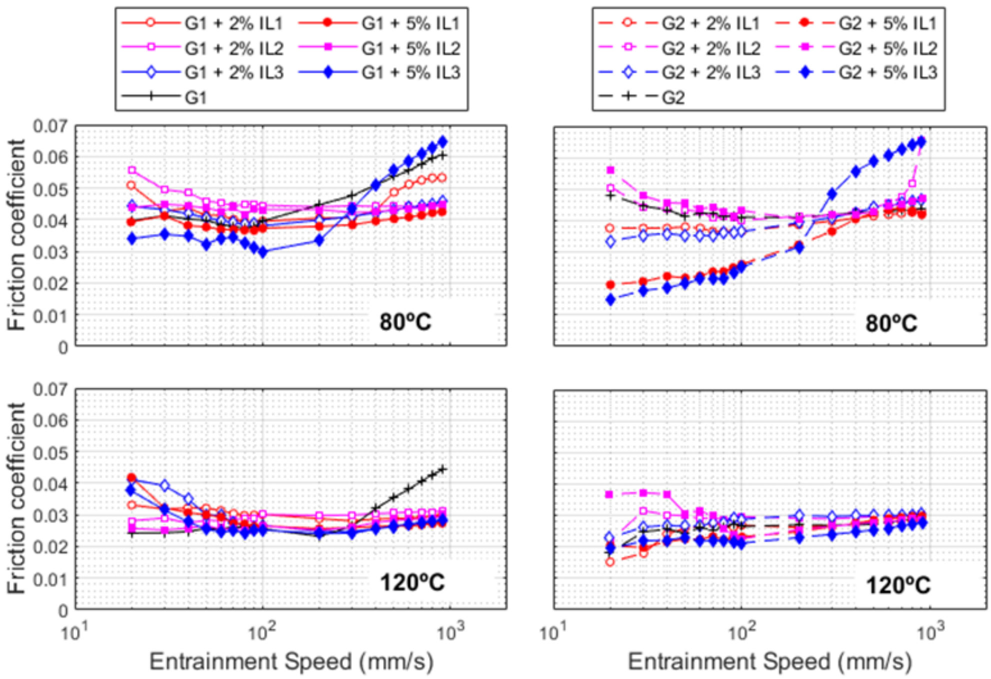


Figure 6. Stribeck curves of the greases and their mixtures with IL1.

4. Conclusions

Three cation phosphonium-derived ILs were used as additive to lithium and calcium-based greases. Rheological properties, lubricant film forming capacity and Stribeck curves of the base greases and their blends with each of the ILs were determined and the following main conclusions could be drawn:

- All calcium-based grease (G2) blends have shown lower viscosity at any shear rate when compared to the lithium-based grease (G1) blends. Generally, the higher is the ILs concentration the higher is the yield stress reduction. This behavior was more evident for the blend of the calcium-based grease with IL3.
- The storage modulus (G') and the loss modulus (G''), and hence the shear stress for which $\tan\delta = 1$, decreased their values with the addition of IL1 and IL3 to the base greases, while the addition of IL2 barely affected these rheological parameters.
- The addition of the ILs to the base greases affected the lubricant film thickness at increasing temperature and mainly in the low speed region. The IL3 had the highest influence on the lubricant film thickness, especially when blended with the anhydrous calcium-based grease.
- The additivation of both greases with the ILs resulted in slightly lower friction results for both temperatures and the tested speed range. This could be mainly related to the lower viscosity of the blends in comparison with the base greases.

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