

Tribology of confined Fomblin-Z perfluoropolyalkylethers: molecular weight dependence and comparison between unfunctionalized and telechelic chains

Marina Ruths^{*,**} and Steve Granick^{**}

Department of Materials Science and Engineering, University of Illinois, Urbana, IL 61801, USA

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The dynamic shear properties of molecularly-thin films of unfunctionalized and end-functionalized (telechelic) Fomblin-Z perfluoropolyalkylether (PFPAE) melts with number-average molecular weight $M_n \approx 3000\text{--}4000 \text{ g mol}^{-1}$ have been studied at shear rates of $10^{-2}\text{--}10^5 \text{ s}^{-1}$ at normal pressures of 1 and 3 MPa. The shear responses are compared to measurements on end-functionalized polymers of the same chemical composition but lower molecular weight, $M_n \approx 2000 \text{ g mol}^{-1}$. The predominantly elastic response and high shear moduli of the confined film of unfunctionalized polymer, Fomblin Z03, suggest that it forms a structure likely to solidify already at low pressure. Its lubricating properties are less favorable than the ones found for hydroxyl- (DOL) and piperonyl-terminated Fomblin-Z (AM2001, AM3001), where associated molecules form a structure less prone to solidification under confinement. The thickness of the compressed films of the end-functionalized polymers increased more strongly with molecular weight than as $M_n^{0.5}$. The shear moduli were found to be larger, the higher the molecular weight, indicating slower relaxations. At a normal pressure of 3 MPa, these films solidified and displayed stick-slip as seen already at 1 MPa in the Z03 film. The limiting shear stress of the unfunctionalized Z03, $\sigma > 3 \text{ MPa}$, exceeded by an order of magnitude the limiting shear stress of all of the end-functionalized polymers. The limiting shear stress of the hydroxyl-terminated polymer was larger than that of the piperonyl-terminated polymer.

Keywords: rheological properties, molecular weight dependence, unfunctionalized Fomblin-Z, end-functionalized Fomblin-Z

1. Introduction

It has been established empirically that the introduction of polar additives [1,2] or polar end-groups [3–20] to perfluorinated polyalkylethers (PFPAE) improves their lubricating properties and their ability to protect a surface against wear. Several types of end-functionalized (telechelic) perfluoropolyalkylethers are utilized in commercial magnetic storage devices (computer disk drives) [3–24]. These lubricant films are applied by a dipping process and the resulting film thickness is a function of the polymer concentration in solution and the withdrawal rate [19,20,24]. A fraction of the molecules in the lubricant film can be covalently bound to a carbon overcoat on the hard-disk by thermal treatment [3–9,11–13,16,20], which improves the stability of the film against wear and humidity.

In order to obtain a large storage capacity per area, the distance between the reading/recording head of the magnetic storage device and the disk surface needs to be small. During so-called “contact recording”, lubricants thus have to work in a very strongly confined film (with a thickness of

only a few tens of ångströms) at very large shear rates (up to $10^9\text{--}10^{10} \text{ s}^{-1}$) [3,20,21,25]. They must also function at low shear rates during startup and stop of the spinning of the disk [3,20,21,25]. The rheological properties of the polymers at the molecular level become crucial at such low film thicknesses.

In this study, we have investigated the thin-film rheological properties of one unfunctionalized and two end-functionalized linear Fomblin-Z perfluoropolyalkylethers of similar number-average molecular weight ($M_n \approx 3000\text{--}4000 \text{ g mol}^{-1}$). The end-functionalized polymers, which were terminated with hydroxyl or piperonyl groups, are currently used as lubricants on commercial hard-disks [3–24]. Since the polymer chains are very short, the effects of the polar end-groups are large and can even dominate the behavior of the polymer in the bulk [26,27]. The purpose of our investigation was to explore the role of polymer molecular weight by comparing the shear response of confined thin films of these polymers to those from a prior study on chains of lower molecular weight [28]. By using a surface forces apparatus modified for oscillatory shear measurements on confined films of thicknesses corresponding to molecular dimensions, we find that the minimum film thickness and the lubricating properties show a distinct dependence not only on the functional end-groups, but also on the molecular weight.

* Present address: Max-Planck-Institut für Polymerforschung, Ackermannweg 10, D-55128 Mainz, Germany.

** To whom correspondence should be addressed.

2. Materials and methods

2.1. Perfluoropolyalkylethers

The Fomblin-Z samples were obtained from Ausimont. The structures of the linear Fomblin-Z backbone and the end-groups are shown in table 1 together with some parameters describing each sample. The polydispersity (ratio of weight-average to number-average molecular weight, M_w/M_n) of these polymers is around 1.1–1.2 [23,29]. The thicknesses of the compressed confined films at different pressures were obtained from force measurements, as shown in figure 1. Measurements on the lower molecular weight DOL and AM2001 samples have been described previously together with a detailed account of the experimental conditions [28].

In order to remove possible dust particles and humidity, approximately 1 ml of the Z03 and DOL samples were dissolved in approximately 10 ml of a hydrofluoroether, HFE-7100 ($C_4F_9OCH_3$, nonafluoro-1-methoxybutane, a product of 3M Corp.), and kept over molecular sieves (Aldrich, pore size 5 Å) overnight. The solutions were then filtered through a Millex-SR syringe filter (Millipore, pore size 0.5 μm) and the solvent evaporated under vacuum at room temperature for 48 h. It was found that solutions of AM2001 and AM3001 in HFE-7100 caused discoloration of the molecular sieves. The use of sieves was thus avoided for these samples, which were only dissolved in HFE-7100, filtered, and dried under vacuum, as described above.

2.2. Measurements of static and dynamic interactions

The investigations of film thicknesses, interaction forces, and thin-film rheology were done with a surface forces apparatus (SFA) built in our laboratory, modeled after the “Mark II” SFA [30] and equipped with a device for oscillatory lateral shear [31–33]. All experiments were done at 25 °C. The surfaces used were thin sheets of muscovite mica, which were silvered on one side and glued with the silvered side down onto fused silica disks with a half-

cylindrical surface with a mixture of dextrose and galactose, as described previously [28]. The separation between the mica surfaces was measured by multiple beam interferometry [34].

During the experiment, the chamber of the instrument was kept dry by exposing the atmosphere to a reservoir of P_2O_5 . After calibration of the contact between the mica surfaces in dry air (defined as zero distance, $D = 0$), a drop of dried polymer was inserted between the separated surfaces with a clean and dry pipette. The experiments were started approximately 0.5–1 h after inserting the drop and finished within 3–4 h.

The samples were slightly viscous, which might cause time effects during approach and separation of the surfaces if the measurements were not equilibrated [35]. The waiting time between the displacement of the base of the spring supporting one of the surfaces and the subsequent measurement of surface separation was varied so that data points at large separations (>1000 Å) were measured approximately 1 min after a displacement of ca. 150 Å. As the separation was decreased, the distance change per step was decreased somewhat and the waiting time was increased successively so that the points where $F/R \approx 0$ in figure 1 were measured at waiting times of a few minutes, the points at the beginning of the repulsive regime (50–120 Å from the final hard-wall separation indicated in figure 1) with waiting times of 10–15 min, and the points close to and on the “hard wall” at approximately 20 min intervals (also on separation). The movement of the surfaces was found to have stopped completely during the times chosen. The waiting times will be discussed further below.

The dynamic (oscillatory lateral shear) measurements were performed with a device described in detail elsewhere [31–33]. The experiments were done in the frequency range of $f = 0.13$ –130 Hz and with a shear displacement amplitude of 0.2–2000 Å. The pressure in the direction normal to the surfaces, P_{\perp} , was controlled with the standard distance controls of the surface forces apparatus [30].

Table 1
Properties of Fomblin-Z perfluoropolyalkylethers with the general structure $E-CF_2O-(CF_2CF_2O)_m-(CF_2O)_n-CF_2-E$.

| Sample | End groups, -E | m/n^a | Functionality ^a | M_n^a (g mol ⁻¹) | Film thickness (Å) | Viscosity ^b (P) | Limiting shear stress (MPa) | |
|--------|---|---------|----------------------------|-----------------------------------|-----------------------|-------------------------------|-----------------------------|---------------------|
| | | | | | | | $P_{\perp} = 1$ MPa | $P_{\perp} = 3$ MPa |
| Z03 | -F | 0.78 | (1.00) | 2900 | 28 | 0.52 (298 K), 0.34 (315 K) | 3 | |
| DOL | -CH ₂ OH | 1.12 | 0.96 | 2100 | 33 ^c | 1.85 (290 K), 0.733 (313 K) | 0.15 | 0.15 |
| DOL | -CH ₂ OH | 0.65 | 0.94 | 4000 | 66 | 2.44 (290 K), 1.207 (313 K) | 0.2 | 0.2 |
| AM2001 | -CH ₂ OCH ₂ C ₆ H ₃ OOCH ₂ | 1.00 | 0.96 | 2300 | 40 ^c | 1.03 (299 K), 0.53 (314 K) | 0.01 | 0.1 |
| AM3001 | -CH ₂ OCH ₂ C ₆ H ₃ OOCH ₂ | 1.43 | 0.95 | 2800 | 73 | 1.42 (291 K), 0.55 (314.5 K) | 0.01 | 0.02 |

^a Characterized at Hitachi Corp. by NMR.

^b Characterized at Hitachi Corp. by capillary viscometry (Ubbelohde viscometer).

^c From [28].

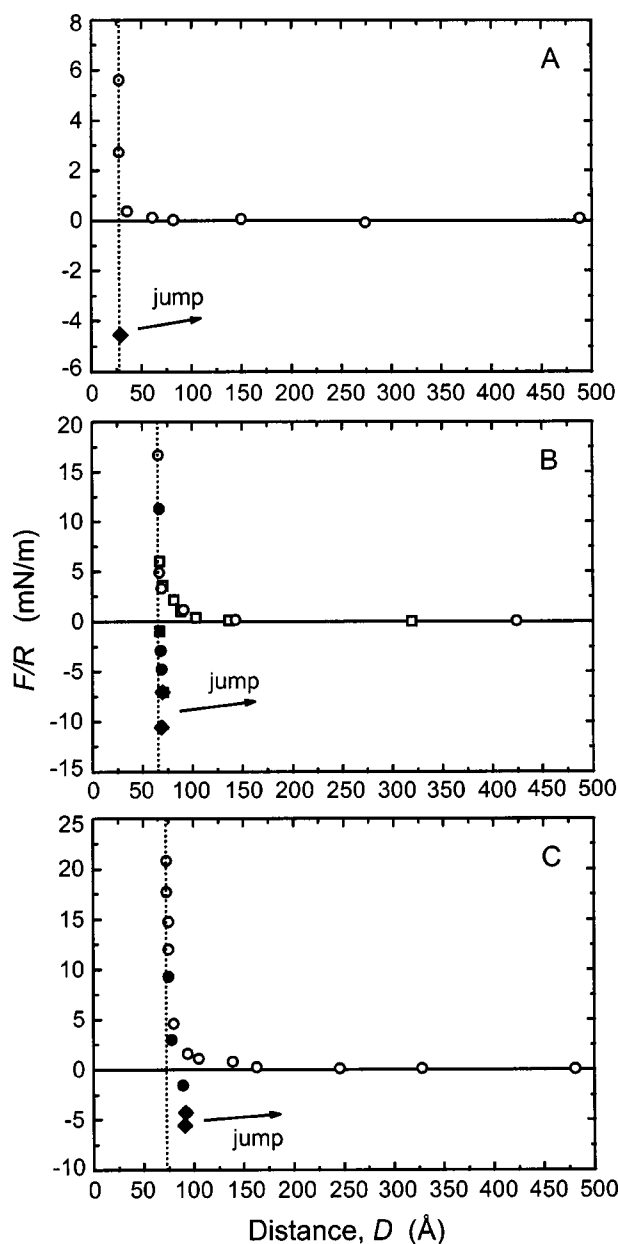


Figure 1. Static force–distance measurements. The force, F (normalized by the radius of curvature of the undeformed surfaces, R) is plotted as a function of separation distance, D , for (A) Fomblin Z03, $M_n = 2900 \text{ g mol}^{-1}$, (B) DOL, $M_n = 4000 \text{ g mol}^{-1}$, and (C) AM3001, $M_n = 2800 \text{ g mol}^{-1}$. Open symbols denote approach and filled symbols separation of the opposed surfaces. For all samples, repulsion is seen on approach and adhesion is seen on separation after prior compression. The points of spontaneous jump apart upon separation are indicated by diamonds. The final thickness obtained on squeezing of the film (“hard-wall repulsion”) is indicated by the dotted vertical lines at 28, 66, and 73 Å in panels (A), (B), and (C), respectively. In figures 1–10, squares and circles show results from independent experiments on different pairs of mica surfaces.

3. Results

3.1. Force measurements

The static interaction forces (normalized by the mean radius of curvature of the undeformed solid surfaces, R) are

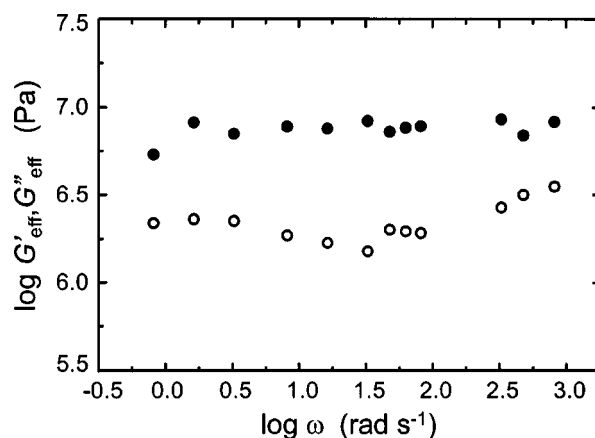


Figure 2. The effective storage modulus (G'_{eff} , filled symbols) and loss modulus (G''_{eff} , open symbols), measured in the regime of linear viscoelastic response for Fomblin Z03 at relatively low pressure in the normal direction, 1 MPa, are plotted on log–log scales as a function of the angular frequency of oscillatory shear, ω . The film thickness was 31 Å, close to the hard-wall thickness indicated in figure 1(A).

plotted against film thickness in figure 1 for Fomblin Z03, the higher molecular weight DOL (cf. table 1) and AM3001. Care was taken to equilibrate these measurements, as described in section 2. Force measurements for the low molecular weight DOL and AM2001 (cf. table 1) are shown in [28]. For all samples, a monotonic repulsion and a final, incompressible layer were seen on approach. This “hard-wall” film thickness was 28, 66, and 73 Å, respectively, as listed in table 1, for the samples in figure 1 (A)–(C). For all the telechelic polymers studied, including the lower molecular weights [28], the monotonic repulsion started at a distance of 100–120 Å from the final hard-wall separation. However, for the unfunctionalized sample, Fomblin Z03, the repulsion began at a smaller distance of only 45–50 Å from the hard wall.

On separation, adhesion was observed. The confined layers were found to expand to a thickness of 29, 69, and 92 Å (figure 1 (A)–(C)), respectively, before the jump apart from the point where dF/dD exceeded the spring constant of the spring supporting one of the surfaces. Adhesion of different strengths was observed for the different samples and the magnitude will be discussed further below.

3.2. Oscillatory shear: regime of linear response

The response of the confined films to small-amplitude oscillatory shear is presented on log–log scales in figures 2–4 as the elastic and viscous shear moduli plotted against angular frequency ($\omega \equiv 2\pi f$, $f = 1.3\text{--}130 \text{ Hz}$). The effective shear moduli, $G'_{\text{eff}}(\omega)$ and $G''_{\text{eff}}(\omega)$, were obtained by normalizing the shear forces in-phase and out-of-phase with the applied deformation by the contact area (measured from the interference pattern observed in the spectrometer) and amplitude, and multiplying by the film thickness. The shear amplitude was a few ångströms, small enough to maintain linear viscoelastic response. At a low normal pressure of $P_{\perp} = 1 \text{ MPa}$, the film thicknesses (given in

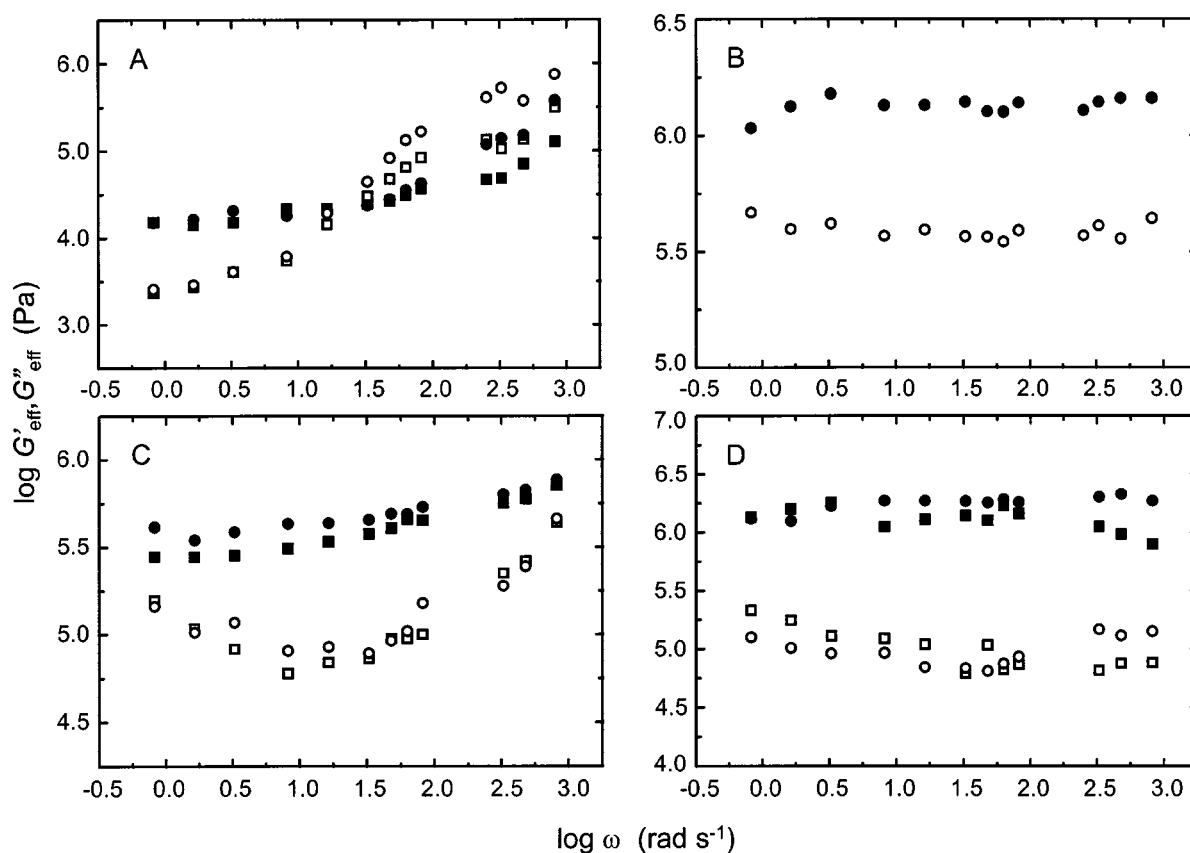


Figure 3. Comparison of the linear viscoelastic response of the hydroxyl-terminated Fomblin-Z (DOL) at two different normal pressures. The effective storage modulus (G'_{eff} , filled symbols) and loss modulus (G''_{eff} , open symbols), measured in the regime of linear viscoelastic response, are plotted on log–log scales as a function of the angular frequency of oscillatory shear, ω . Panels (A) and (B) show data for $M_n = 2100 \text{ g mol}^{-1}$ at a normal pressures of 1 and 3 MPa, respectively. Panels (C) and (D) show the corresponding data for DOL of a higher molecular weight, $M_n = 4000 \text{ g mol}^{-1}$. In panels (A) and (B), the film thickness was 34 and 33 Å, respectively. For the sample of higher molecular weight (panels (C) and (D)) the film thickness was 67–70 and 66 Å, respectively. The quoted film thicknesses at higher pressure are the hard-wall thickness measured for each sample (cf. table 1).

the figure legends) were only slightly larger than the “hard-wall” thickness for these samples that were observed at a pressure of $P_{\perp} = 3 \text{ MPa}$ (cf. hard-wall film thicknesses from force measurements in table 1).

At the relatively low pressure of 1 MPa, the viscoelastic response of the unfunctionalized Fomblin Z03 film (figure 2) was dominated by the elastic component at all frequencies studied, which indicates that these frequencies exceeded the inverse longest relaxation time for the confined polymer to flow. The response of this sample was thus strongly rubber-like, with high, frequency-independent moduli, as has been observed also for other confined linear polymers in this frequency regime [33,36,37].

There are significant differences in the shear responses observed for the unfunctionalized and telechelic polymers. The magnitudes of the moduli for the telechelic polymers at this pressure (figures 3 (A), (C) and 4 (A), (C)), and also at the higher pressure of 3 MPa (figures 3 (B), (D) and 4 (B), (D)), were considerably lower.

For the low molecular weight hydroxyl-terminated DOL at a normal pressure of 1 MPa (figure 3(A)), a region of predominantly elastic response at low frequencies was followed by a mainly viscous response at $\omega > 10 \text{ rad s}^{-1}$. The

effective storage modulus of the low molecular weight DOL at this pressure was two orders of magnitude lower than for the unfunctionalized Z03 (figure 2). This result is significant because the elastic shear modulus is closely linked to the static friction encountered upon startup of sliding.

The higher molecular weight DOL showed a predominantly elastic response at a pressure of 1 MPa (figure 3(C)), with larger moduli than the lower molecular weight DOL (figure 3(A)). It is reasonable that higher molecular weight should result in slower relaxation. As a result of this shift to slower response, the sample of higher molecular weight showed a more rubber-like response than the lower molecular weight over the whole frequency range investigated.

The observation of slower relaxation for higher molecular weight polymer was confirmed in experiments on the piperonyl-terminated AM2001 and AM3001. At a pressure of 1 MPa, the viscoelastic response observed for AM3001 (figure 4(C)) was similar to the one obtained for the lower molecular weight, AM2001 (figure 4(A)), except for that it was shifted towards lower frequencies. The shear moduli observed at the highest frequencies for the sample of lower molecular weight (figure 4(A)) coincided with the shear

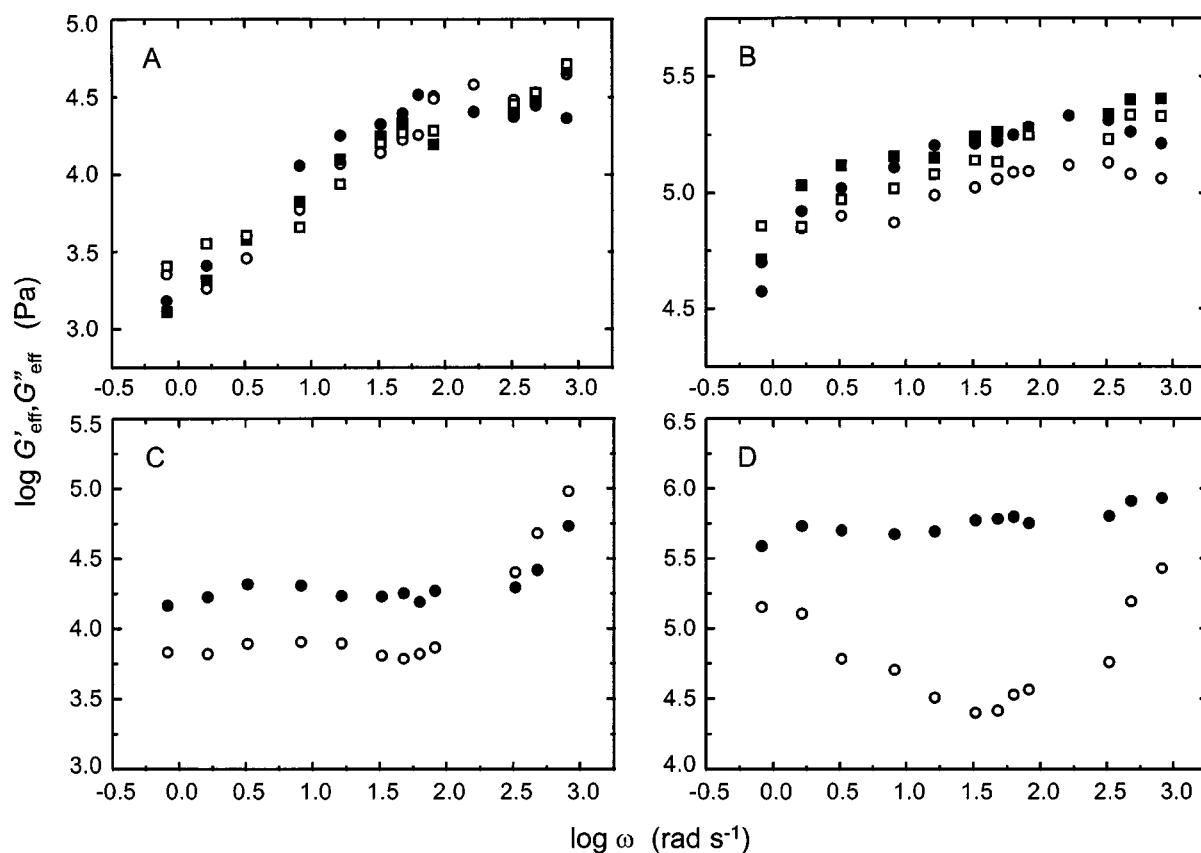


Figure 4. Comparison of the linear viscoelastic response of the piperonyl-terminated Fomblin-Z (AM2001 and AM3001) at two different normal pressures. The effective storage modulus (G'_{eff} , filled symbols) and loss modulus (G''_{eff} , open symbols), measured in the regime of linear viscoelastic response, are plotted on log-log scales as a function of the angular frequency of oscillatory shear, ω . Panels (A) and (B) show data for AM2001 ($M_n = 2300 \text{ g mol}^{-1}$) at the normal pressures of 1 and 3 MPa, respectively. Panels (C) and (D) show the corresponding data for AM3001 ($M_n = 2800 \text{ g mol}^{-1}$). In panels (A) and (B) the film thickness was 42 and 40 Å, respectively. For the sample of higher molecular weight (panels (C) and (D)) the film thickness was 79 and 74 Å, respectively.

moduli observed at the lowest frequencies for the sample of higher molecular weight (figure 4(C)).

A similar effect was observed as the normal pressure was increased from 1 to 3 MPa (figures 3 and 4): Both an increase in normal pressure and an increase in the molecular weight of the polymer slowed down the viscoelastic response of the confined films.

3.3. Non-linear shear moduli

The transition from linear to non-linear viscoelastic response as the input amplitude was increased is shown in figures 5–7. Here the elastic and viscous moduli of the films are plotted as functions of effective strain (deformation amplitude divided by film thickness) at $f = 1.3 \text{ Hz}$. Even if the motion in response to sinusoidal oscillatory stress is not strictly sinusoidal, which is characteristic of a nonlinear response, the component of response at the same frequency as the fundamental drive solely determines the energy lost during the cycle of deformation [37]. For this reason, we analyzed the non-linear responses at the fundamental frequency (i.e., at the same frequency as the forcing frequency).

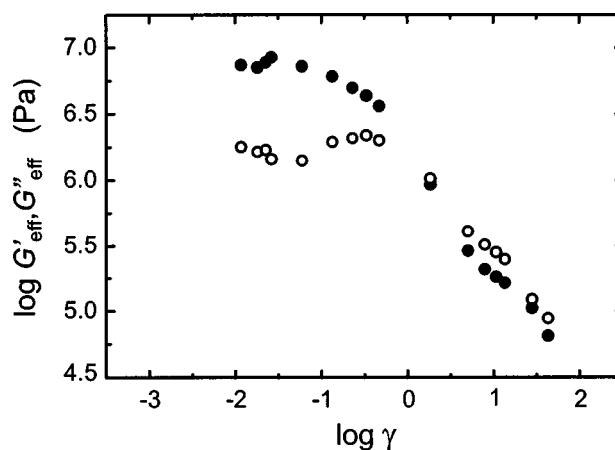


Figure 5. Strain dependence of the shear response of Fomblin Z03. The effective storage modulus (G'_{eff} , filled symbols) and loss modulus (G''_{eff} , open symbols) are shown as a function of the effective strain (deformation amplitude divided by film thickness) as the amplitude of the oscillatory shear was increased. The experiments were performed at low pressure, 1 MPa, at a frequency of 1.3 Hz. The film thickness was the same as in figure 2. We observed a discontinuous transition from linear to non-linear viscoelastic response, which indicates stick-slip sliding.

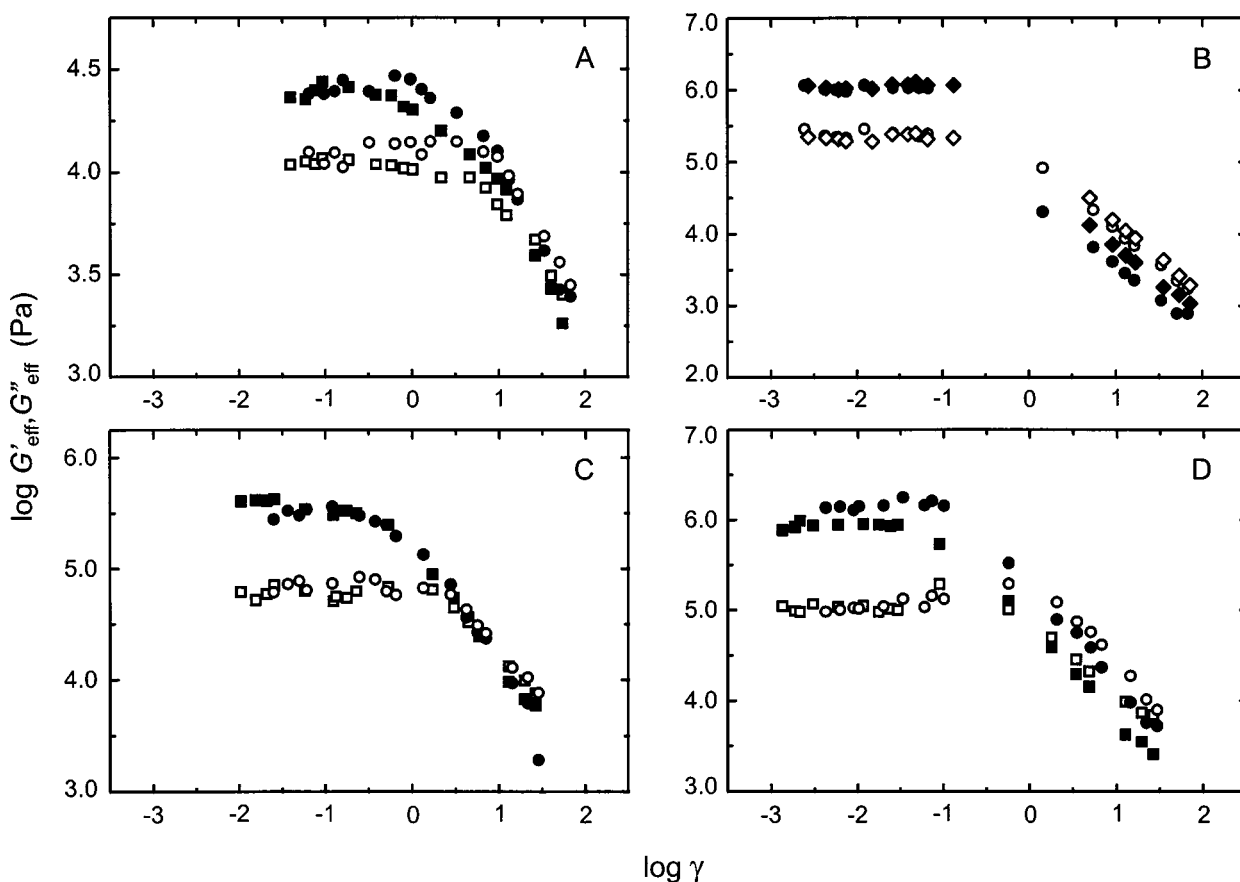


Figure 6. Strain dependence of the shear response for the hydroxyl-terminated DOL. The effective storage modulus (G'_{eff} , filled symbols) and loss modulus (G''_{eff} , open symbols) are shown as a function of the effective strain as the input amplitude of the oscillatory shear was increased. The experiments were performed at a frequency of 1.3 Hz using the sample with $M_n = 2100 \text{ g mol}^{-1}$ at pressures of 1 and 3 MPa (panels (A) and (B), respectively), and similarly for the sample with $M_n = 4000 \text{ g mol}^{-1}$ (panels (C) and (D)). The diamond symbols in panel (B) show results from an additional experiment at 130 Hz. The film thicknesses were the same as in figure 3. A discontinuous transition from linear to non-linear viscoelastic response, which indicates stick-slip sliding, was seen at the higher pressure for both samples, whereas the transition at the lower pressure was continuous (smooth sliding).

In the experiments in figures 5–7, the film thicknesses were the same as for the measurements shown in figures 2–4. At low deformation amplitude (low strain), all samples showed a linear viscoelastic response in accordance with the measurements at low deflection amplitude in figures 2–4.

At a low pressure of 1 MPa, the transition from linear to non-linear response occurred at the lowest strain, $\gamma = 0.5$ ($\log \gamma = -0.3$), for the unfunctionalized Z03 (figure 5) and at the highest strain, $\gamma \approx 3$ ($\log \gamma = 0.5$), for the low molecular weight DOL (figure 6(A)). The transition was discontinuous for the Z03 film (indicating that the commencement of macroscopic-sized sliding in this system occurred as a slip) and continuous for the other samples (figures 6 (A), (C) and 7 (A), (C)). The decrease in moduli after the transition indicates shear thinning. At higher pressure, 3 MPa, also the hydroxyl- and piperonyl-terminated polymers showed a discontinuous transition from linear to non-linear response (figures 6 (B), (D) and 7 (B), (D)) at a strain of approximately 0.1 ($\log \gamma = -1$).

The common observation in all of these measurements was that with increasing input amplitude, a predominantly

elastic response (small deformation) gave way to a predominantly viscous response (large deformation). The following section analyzes the viscous stress explicitly.

3.4. Limiting shear stress

A plateau of viscous shear stress – a so-called limiting shear stress – is commonly observed in lubricated systems when the shear rate is sufficiently large [37,38]. In figures 8–10, the viscous responses shown as shear moduli in figures 5–7 are presented as the shear stress (force normalized by area) as a function of effective shear rate (strain \times angular frequency). In the region of linear response, the stress increased linearly with shear rate, as expected. In the non-linear regime, the shear stress increased much more slowly with shear rate, and the limiting value of the shear stress at the transition from linear to non-linear response differed between samples.

The unfunctionalized Z03 (figure 8) showed the highest limiting shear stress; a final, constant value was not reached at the shear rates investigated, and only a lower bound of 3 MPa can be given (cf. table 1).

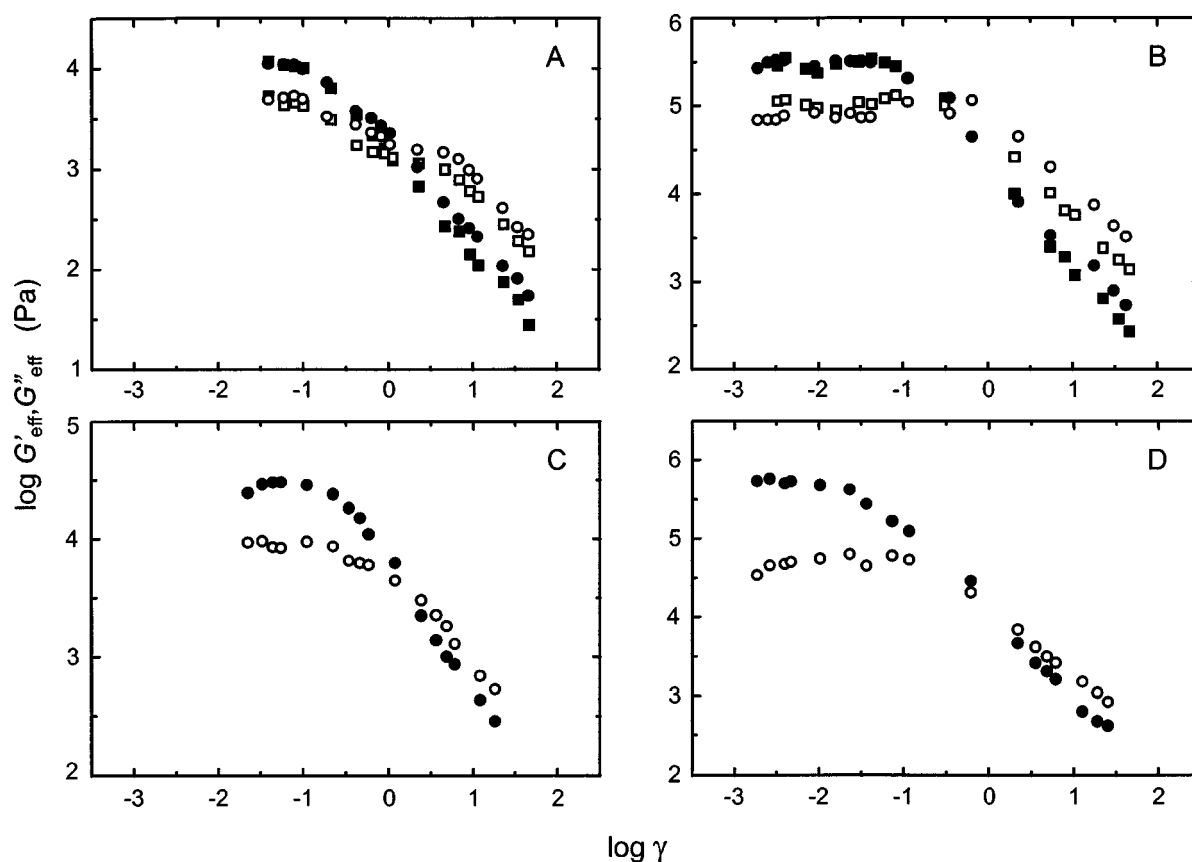


Figure 7. Strain dependence of the shear response for the piperonyl-terminated AM2001 and AM3001. The effective storage modulus (G'_{eff} , filled symbols) and loss modulus (G''_{eff} , open symbols) are shown as a function of the effective strain. The experiments were performed at a frequency of 1.3 Hz for AM2001 ($M_n = 2300 \text{ g mol}^{-1}$) at pressures of 1 and 3 MPa (panels (A) and (B), respectively), and similarly for AM3001 ($M_n = 2800 \text{ g mol}^{-1}$, panels (C) and (D)). The film thicknesses were the same as in figure 4. A discontinuous transition from linear to non-linear viscoelastic response (indicative of stick-slip sliding) was seen at the higher pressure, whereas the transition was continuous at the lower pressure.

The limiting shear stresses of the telechelic polymers were more than an order of magnitude lower and showed very little dependence on molecular weight. For the hydroxyl-terminated DOL (figure 9), the magnitude of the limiting stress, around 0.2 MPa, was unaffected by pressure within the regime investigated. For the piperonyl-terminated polymers (figure 10) the limiting stress at low pressure was 0.01 MPa, an order of magnitude lower than for the DOL samples. At increased pressure, the lower molecular weight, AM2001 (figure 10(B)), responded with an increase in stress to a value similar to the low molecular weight DOL, while the stress for AM3001 (figure 10(D)) remained low.

4. Discussion

4.1. Normal forces, film thickness, and adhesion

On compressing these films, a repulsive force was measured approximately 50 \AA from the final hard-wall separation for the unfunctionalized Z03 (figure 1(A)). For the end-functionalized chains, the repulsion started at a larger separation of $100\text{--}120 \text{ \AA}$ from the hard-wall for each sample (figure 1 (B) and (C)). Similar results were obtained

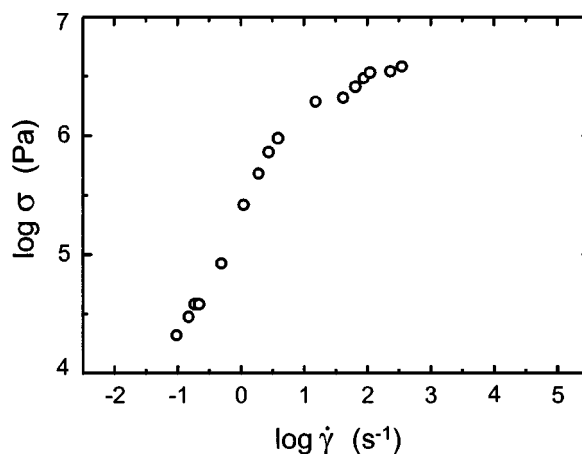


Figure 8. The data for the loss modulus of Fomblin Z03 in figure 5, shown as viscous stress (force divided by area) vs. shear rate (strain multiplied by angular frequency). The film thickness was 31 \AA . A limiting stress was reached at a strain (cf. figure 5) of approximately 0.5.

also for the low molecular weight hydroxyl- and piperonyl-terminated samples [28]. The phenomenon that one cannot squeeze out all of the polymer – that a final, incompressible film is seen, a “hard wall” – is commonly observed when two solids are separated by a polymer melt [33,35–41] and

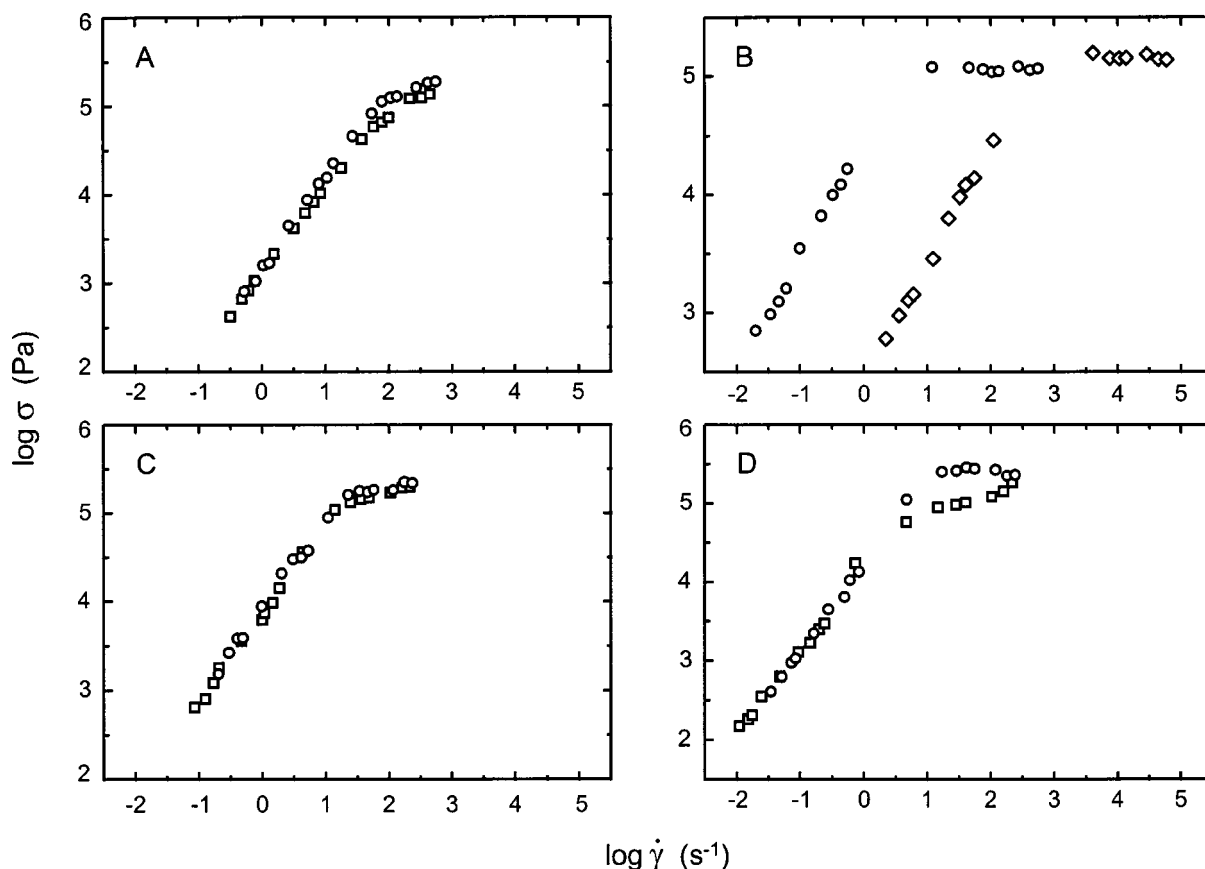


Figure 9. The data for the loss modulus of the hydroxyl-terminated DOL in figure 6, shown as viscous stress vs. shear rate. As in figure 6, the diamond symbols in panel (B) show results from an additional experiment at 130 Hz. For the sample of lower molecular weight, a limiting stress was reached at a strain (cf. figure 6) of approximately 3 at the pressure of 1 MPa (A) and 0.1 at 3 MPa (B). For the higher molecular weight (panels (C) and (D)), a limiting stress was reached at strains of 1.6 and 0.1, respectively.

is believed to occur because the relaxation time exceeds the experimental time or because of pinning of the polymer to the solid surfaces [42].

When interpreting the repulsive forces measured at larger separations than the hard wall, it is reasonable to question whether the equilibration time was sufficiently long. The equilibration times chosen (cf. section 2 and [28]) should have been sufficient to avoid time effects explainable by the bulk viscosity of the polymer [35]. However, the relatively long-ranged repulsion observed for all telechelic samples possibly reflects physisorption of end-groups to the polar mica, so that a much longer equilibration time than expected from bulk viscous flow alone would have been necessary to remove these polymers from the gap between the surfaces.

Although the high viscosity of the samples made it more difficult to measure the adhesion, these measurements could be done provided that the time between the change in separation distance and the subsequent measurement was sufficiently long. The adhesion measured upon slow separation of the surfaces differed markedly between different samples. In a previous study of several low molecular weight telechelic Fomblin-Z polymers [28], it was shown that the adhesion did not correlate with the bulk viscosity or the film thickness. Instead, the largest value was obtained

for a DOL sample (the low molecular weight DOL in the present study) with a viscosity and film thickness intermediate to those of polymers of similar molecular weight but with other functional end-groups [28]. The DOL polymers showed the largest adhesion also in the present study (where they also, incidentally, have the largest bulk viscosity).

Interestingly, no significant dependence of the adhesion on the molecular weight (film thickness) was observed for either of the samples. The van der Waals attraction ($F/R = -A_H/6D^2$, where the Hamaker constant calculated according to van der Waals–Lifshitz theory [43] is $A_H = 2.47 \times 10^{-20}$ J for mica interacting across Fomblin-Z with $\epsilon = 2.03$ and $n = 1.294$ [44]) is very small at the separations, where adhesion was observed in these systems and cannot account for the values measured. Due to the long equilibration times, the film had in general been compressed for about 1 h before the separation occurred. During this time, reorganization of the chains within the confined film may occur, producing layering or bridging between the surfaces, and this could explain why adhesion appeared upon separation even though no attraction was seen on approach. We will return to the possible explanations for the adhesion after discussing possible structuring within the film.

Force measurements have been performed in a similar manner on other unfunctionalized Fomblin-Z samples:

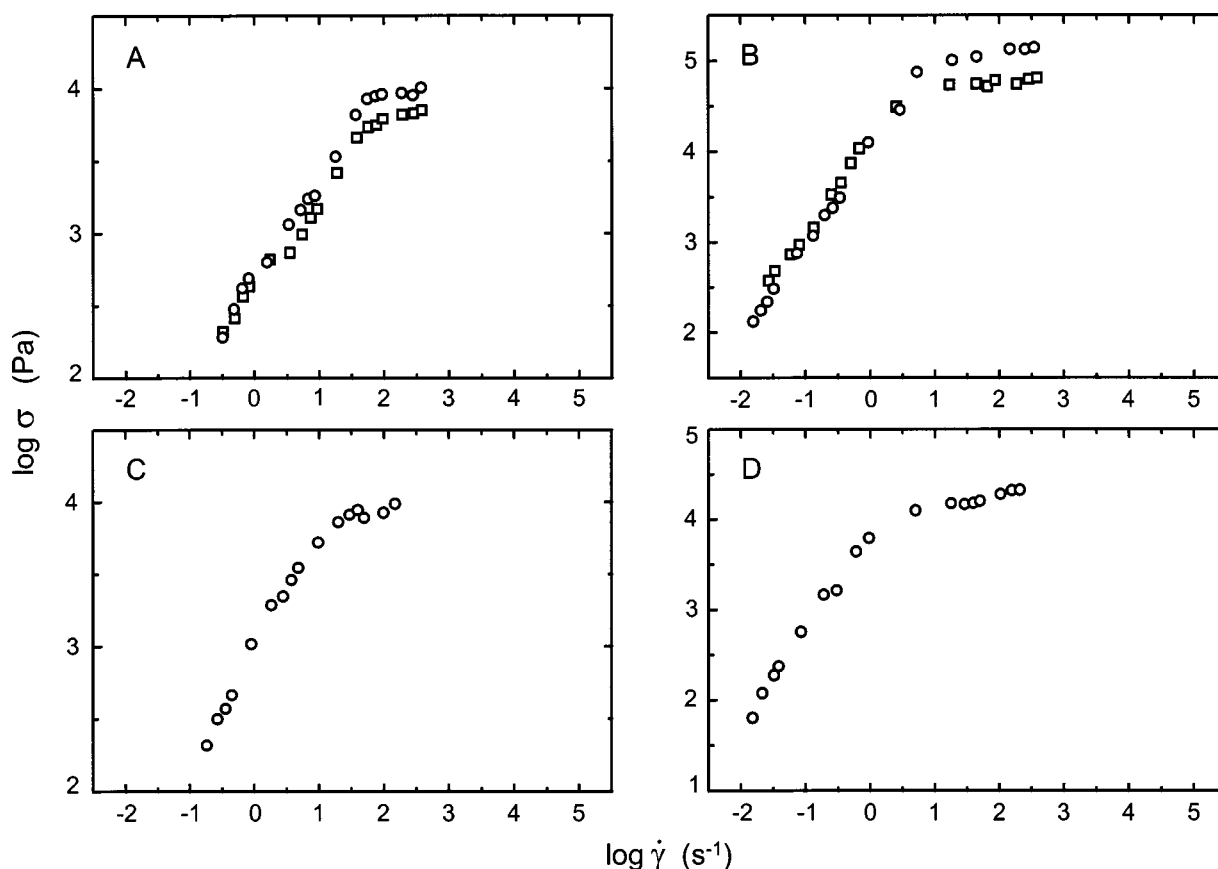


Figure 10. The data for the loss modulus of the piperonyl-terminated Fomblin-Z in figure 7, shown as viscous stress vs. shear rate. For the lower molecular weight, AM2001, a limiting stress was reached at a strain (cf. figure 7) of approximately 2 at a normal pressure of 1 MPa (panel (A)) and 0.1 at a normal pressure of 3 MPa (panel (B)). For the higher molecular weight, AM3001 (panels (C) and (D)), a limiting stress was reached at strains of 0.6 and 0.1, respectively.

a sample with a molecular weight around $10\,000\text{ g mol}^{-1}$ [45]; and a sample with $M_n = 12\,800\text{ g mol}^{-1}$ [39]. In those measurements, the repulsion observed on approach appeared at a distance of approximately 50 \AA from the hard-wall film thickness of around 30 and 90 \AA [39], respectively. The presence of a layering in the confined films may be inferred for molecular weights of $10\,300$ and $12\,800\text{ g mol}^{-1}$, where the film thickness decreased during shear at large pressures from 90 \AA to a final thickness of 26 \AA in steps of 8 \AA [39,40], which is close to the estimated molecular segment diameter of 7 \AA [4,14,46,47]. We did not observe any decrease in the layer thickness of 28 \AA for the unfunctionalized polymer in our study, even at pressures slightly larger than in figure 1(A). This film thickness might, however, correspond to an integer number of segment diameters.

The hard-wall film thicknesses of the lower molecular weight hydroxyl- and piperonyl-terminated Fomblin-Z (table 1 and [28]) are within the possible distance range of layered structures of the kind observed in simple liquids [43] and in linear polydimethylsiloxane [48] confined between mica surfaces, but no decrease in separation was observed when the normal pressure was raised above 3 MPa. The film thicknesses measured for the higher

molecular weight DOL and AM3001 probably exceed the extension of a layered structure (generally at most 8–10 segment diameters), and no significant decrease in film thickness was observed at higher pressure for these samples either. In all cases, the thickness of the confined film was substantially smaller than the extended length of the polymer chain (ca. 70 and 140 \AA for $M_n = 2000$ and 4000 g mol^{-1} , respectively [49]); this is a reasonable result since one would expect the chains in the melt to take a structure closer to a random coil. However, for the hydroxyl- and piperonyl-terminated samples in our study, the film thickness increased more strongly with molecular weight than as the $M_n^{0.5}$ dependence expected for a random coil, and also more strongly than the $M_n^{0.6}$ dependence observed in spreading experiments of DOL on an amorphous carbon surface [23,24].

Previous experiments on several lower molecular weight telechelic Fomblin-Z polymers suggest that associated structures form in these materials [28] due to the polarity of the end-groups. Under such circumstances the film thickness cannot be expected to follow predictions for neutral polymer. The polar interactions in the hydroxyl-terminated Fomblin-Z are further enhanced compared to in the piperonyl-terminated due to its capacity for hydrogen

bonding, which is also reflected in the differences in bulk viscosity measured for these two systems compared to the unfunctionalized (table 1).

The film thickness measured for the unfunctionalized polymer, combined with the observations in the literature [39,40] on layering of higher molecular weight unfunctionalized Fomblin-Z, suggest that the adhesion in this system might represent an adhesive minimum in a layered structure. Such layering might be hindered in the telechelic polymers due to association of the polar end-groups. In a previous study [50] on rate-dependent adhesion, it was suggested that bridging of physisorbed DOL from one surface to the other might occur, and this is a possible explanation for the stronger adhesion observed with the end-functionalized polymers.

The magnitude of the bridging attraction has been estimated [51] for a polymer melt system consisting of two surfaces covered with telechelic “brushes” (chains with both end-groups attached to one surface) of height h and a fraction of bridging chains (expressed as a surface coverage σ_b). Our systems are more complicated than this model, since the confined films may contain some chains that do not have their end-groups in contact with the surfaces. However, using this model, the bridging free energy per area at a separation of $2h$ is given by $\Delta E = k_B T (r_0/h)^2 \sigma_b$, where r_0 is the unperturbed end-to-end distance of the polymer chain and r_0/h a stretching ratio [51]. We estimate that $r_0/h \approx 1$ (the chains are not strongly stretched from the surfaces). In contact at $D = 2h$ (i.e., at the film thicknesses given in table 1), the interaction areas can be calculated from the “chord theorem” [43], $A = 2\pi R \times 2h$ ($R \approx 1.5$ cm), or estimated from the fringe shapes, as described in section 3. As an example, $A \approx 6 \times 10^{-10}$ m² for the low molecular weight DOL. The volume between the surfaces within this interaction area, approximately $2hA$, contains around 10^9 molecules of which an unknown fraction forms bridges. Assuming that 10–20% of the chains form bridges gives $\sigma_b \approx 2\text{--}4 \times 10^{17}$ m⁻², and using the Derjaguin approximation [43], we obtain $(F/R)_{\text{adh}} = 2\pi\Delta E \approx 5\text{--}10$ mN/m, in reasonable agreement with the adhesion measured in these systems.

4.2. Shear of thin films

The commercially used hydroxyl- and piperonyl-terminated polymers displayed much lower shear moduli and a reduced occurrence of stick–slip at a normal pressure of 1 MPa (i.e., better lubricating properties) compared to the unfunctionalized polymer. In a previous study, we proposed that the explanation at the molecular level of the different shear properties is not necessarily the differences in the interactions between the different polar groups and the solid surface, but the structure throughout the confined film [28]. It has been shown that several linear unfunctionalized polymers [39–41,52] similar to the Fomblin Z03 easily solidify (show rubber-like shear response with large elastic modulus and limiting shear stress) on confinement.

This included high molecular weight Fomblin-Z [39,40] and a different linear perfluoropolyalkylether, Demnum S-20¹, with a molecular weight around 2000 g mol⁻¹ [41].

The associated structure suggested for the hydroxyl- and piperonyl-terminated polymers can tentatively be compared to that of branched perfluorinated chains such as a high molecular weight Fomblin-Y [39] and a Krytox² sample with a molecular weight around 2000 g mol⁻¹ [41]. The branched polymers are more fluidlike, i.e., less prone to solidify at low pressure, and are known to function well as lubricants. It was interesting to note that the Krytox sample [41] showed a similar, unusual frequency dependence of the shear modulus (a predominantly elastic response at the lowest frequencies investigated) as the low molecular weight DOL (figure 3(A)).

The shear moduli, limiting strain and limiting shear stress were higher in the hydroxyl-terminated polymer than in the piperonyl-terminated. This likely reflects the stronger interaction between the hydroxyl-terminated chains due to hydrogen bonding. Larger shear moduli were obtained with increasing molecular weight, which indicates a slower relaxation in the higher molecular weight systems both at low and high pressure. Since the density of polar end-groups is lower for the samples of higher molecular weight, the contribution of association to the shear response of the films might be lower. We did not observe a strong dependence of the limiting strain (deflection amplitude) on molecular weight, likely because the molecular weight was not varied in a sufficiently large range to cause a significant dilution of the end-groups.

4.3. Interactions of end-groups with the solid surface

The end-groups in our study do not have any specific or covalent interaction with the solid surface, but polar end-groups are expected to be located on average close to the polar mica. Models for the dependence of the shear stress on shear rate have been proposed for cases where a polymer interacts either strongly [53,54] or weakly with the surface [55]. In both cases the stress is expected to increase linearly with the shear rate at small deformations (linear response regime), which we also observed experimentally for all our systems. For weak interactions with the confining surfaces, it has been suggested that the stress in the non-linear regime increases as the shear velocity to the power 1/3 [55], while for strong interactions and bridge formation, a plateau in the stress with no dependence on shear velocity or a dependence to the power $-1/3$ is followed by a region of stress increasing as velocity to the power 1/3 [53,54].

Experimentally, we observed that the stress in the non-linear regime for the Fomblin Z03, AM2001, and AM3001 samples increased slowly with shear rate, while an indication of a plateau, followed by a subsequent slow increase,

¹ Demnum is a registered trademark of Daikin Industries.

² Krytox is a registered trademark of E.I. du Pont de Nemours and Company.

was found for DOL. At larger pressure a plateau in the shear stress was seen for DOL, while the stress was still increasing slowly in AM2001 and AM3001.

The performance of a lubricant is, however, determined not only by its friction coefficient (i.e., by its sensitivity to load or pressure) but also by the absolute magnitudes of the friction force and the stability of the film. Upon comparing the hydroxyl- and piperonyl-terminated polymers we find that their behavior was qualitatively similar, with the piperonyl-terminated polymer having lower shear moduli and limiting shear stress.

For practical applications, their different stability towards temperature and moisture also becomes an important consideration. It is known that the piperonyl group easily decomposes to form a hydroxyl group [18]. The considerably larger film thickness obtained for both hydroxyl- and piperonyl-terminated polymers for a moderate increase in molecular weight may be a disadvantage in contact recording where a very thin film is desirable. It is likely that a different film thickness could be created by the dipping process employed in industry [19].

5. Summary

We have measured the rheological properties of thin films of unfunctionalized and end-group-functionalized (telechelic) linear perfluoropolyalkylethers (Fomblin-Z) confined between atomically smooth surfaces. The polymers with polar end-groups showed more favorable lubricating properties than the unfunctionalized, likely reflecting the fact that whereas unfunctionalized chains form a random structure in the bulk, and possibly a layering in a thin film confined between two surfaces, functionalized chains may form structures in which the end-groups associate due to polar interactions for the piperonyl-terminated polymer, and additional hydrogen bonding for the hydroxyl-terminated.

In comparing chains of the same chemical composition but different molecular weight, we found that thicker films with larger shear moduli resulted when the molecular weight was increased from 2000 to 3000–4000 g mol⁻¹. In addition, the stick–slip observed at high pressure was less pronounced for the samples of higher molecular weight. The shear moduli and limiting shear stress of the piperonyl-terminated polymer were lower than those of the hydroxyl-terminated.

It will be desirable to extend these studies to chains of still larger molecular weight, and to seek a better understanding of why the magnitude of the limiting shear stress depends so strongly on chain-end functionality.

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