NANO/MICRO-RHEOLOGY OF PERFLUOROPOLYETHER LUBRICANTS

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ABSTRACT
The bulk rheological properties, such as shear viscosity and storage & loss moduli of perfluoropolyether (PFPE) with different molecular weights and endgroup functionalities were examined via a rotational rheometer. Equilibrium and non-equilibrium molecular dynamics simulations were performed to provide a molecular visualization tool to clearly understand the intrinsic nanostructure as well as to predict the bulk shear viscosity, which reveals a strong dependence on temperature and PFPE molecular architecture.

INTRODUCTION
In current information storage devices, molecularly-thin perfluoropolyether (PFPE) lubricant films are applied on various carbon overcoats for hard disk drive’s reliability and lubrication [1], where the tribological performance due to molecular architecture of the lubricant is one of the critical issues. Using a pin on disk test, the relationship of PFPE tribology and molecular rheology has been reported [2]. In this paper, using a rotational rheometer, we measured the bulk rheological properties of fractionated PFPEs with different molecular weights, endgroup functionalities (Fomblin Z, Zdol, and ZdolTX), as well as temperatures, which provide a complementary tool to examine the lubricant performance. To date, our ongoing equilibrium molecular dynamics (EMD) and non-equilibrium molecular dynamics (NEMD) simulations, with the ease of imposing the molecular architecture, have verified the nanostructure of PFPE system as well as predicted their rheological properties.

EXPERIMENTAL
In our rheology measurement, commercially available PFPEs were used, which contain a chemical structure of X–CF₂[(OCF₂CF₂)m–(OCF₂)n]OCF₂–X (m/n ≅ 2/3). Here, the endgroup, X, stands for F in Z (nonfunctional), CH₂OH in Zdol (functional), and CH₂(OC₂H₄)pOH (on average, p=1.5) in ZdolTX (strongly functional), respectively, where the hydroxyl/ether groups exhibit strong polar interaction. Using rotational rheometers (Physica LS-100 for shear rate of 10⁻⁶ ~ 10⁻³ sec⁻¹ and Physica MC-120 for shear rate of 1,000 ~ 4,000 sec⁻¹), we measured bulk viscosity (η) and storage & loss moduli (G' & G'') at different temperatures (T) via steady shear and dynamic oscillation measurements.

One of the interesting observations is that η exhibits different dependence on weight average molecular weight (Mₘ) due to the difference in endgroup functionality (εb). It is shown in Fig. 1 that η is proportional to Mₘ⁻⁰.₅ for Zdol, whereas a remarkable crossover behavior occurs at a critical Mₘ (Mₙ) for ZdolTX, i.e., η ∝ Mₘ for Mₘ < Mₙ and η ∝ Mₘ² for Mₘ > Mₙ.

![Figure 1. η as a function of Mₘ for functional PFPEs.](image)

![Figure 2. G'' vs. angular frequency (ω) for ZdolTX with Mₘ=4,400 g/mol.](image)
for $M_w > M_c$ with $M_c \approx 3,600$ g/mol, which is probably due to the peculiar lubricant endgroup coupling in the ZdolTX system and thus results in a complex cluster shown in the simulated schematics (Fig. 3). From the T dependence on $\eta$, the activation energy ($E_a$) for PFPE flow was further estimated for various $M_w$, and $\varepsilon^*$, where $E_a$ is found to be dominant by $\varepsilon^*$, not $M_w$.

From our oscillatory experiments, we quantified the viscoelastic properties of PFPE via the complex shear modulus $G'' = G' + iG''$, where $G''$ is strongly dependent on T (Fig. 2), indicating the formation of different microstructures at various T, while $G'$ is weakly dependent on T.

**MOLECULAR SIMULATIONS**

EMD simulations [3] were first performed to examine the structure of PFPE bulk. Figure 3 demonstrates a typical simulated snapshot of functional PFPE system, where clusters of functional endgroups (in red) are responsible for the peculiar rheological response in our experiments. Further, by integrating the so-called SOLLD equation of motion and imposing the Lee-Edwards boundary condition [4], NEMD simulation of static shear was realized at a constant T. By calculating the off-diagonal components of bulk stress tensor, we calculated the shear viscosity. Figure 4 illustrates the shear viscosity as a function of shear rate and molecular weights ($N_p$) for nonfunctional PFPEs ($\varepsilon^* = 0$), where the melt exhibits a high, nearly constant viscosity at a low shear rate (1st Newtonian plateau), then presents a linear decrease with the increase in shear rate, and finally reaches a plateau (Fig. 4(a)) again. Using the Carreau - Yasuda model [5], we found that the power of shear rate ($\dot{\gamma}$) in the shear thinning regime is nearly $-0.6$, i.e., $\eta \propto \dot{\gamma}^{-0.6}$. As well, the zero-shear-rate viscosity ($\eta_0$) linearly increases with $N_p$ in Fig. 4(b). Similar study has been extended to the functional PFPE system and the comparison with experiments will be made.

Additionally, we included $\varepsilon^*$ (Fig. 5 (a)) as well as T (Fig. 5 (b)) dependences into our NEMD simulations, which have shown a very strong effect on the PFPE bulk viscosity. As we increase $\varepsilon^*$, a large $\eta$ is observed. However, $\eta$ does not accord with a simple linear dependence on $\varepsilon^*$. Therefore, we believe that there exists a critical $\varepsilon^*$ range, where a structure mutation occurs in the PFPE bulk and we expect that $\eta$ vs. $\varepsilon^*$ will also have a similar crossover as in Fig. 1. Also, it is seen in Fig. 5(b) that $\eta$ greatly increases as the bulk cools down. Likewise, a nonlinear $\eta$ dependence on T is realized, where a critical temperature is required to overcome the energy barrier $E_a$ to modify the melt structure.

**SUMMARY**

The bulk rheological properties of PFPE were examined via both experiments and theoretical simulations, where the molecular architecture (including molecular weight and endgroup functionality) as well as temperature greatly affects the bulk statics and dynamics. The study of nanorheology of PFPE bulk and nanofilm, including shear and elongation, in conjunction with multiscale modeling is currently underway.

**REFERENCES**