

468b Nano-Rheology of Lubricant Films

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In current information storage devices, molecularly-thin lubricant films, *e.g.*, perfluoropolyether (PFPE) series, are dip-coated onto various carbon overcoats for hard disk drives' reliability and lubrication [1], where the tribological performance due to molecular architecture is one of the critical issues. Using a pin on disk test, the relationship of PFPE tribology and molecular rheology was first discussed [2]. Here, we studied the rheological properties as a complementary tool to estimate the lubricant tribological performance.

Experimentally, using a rotational rheometer, we measured the bulk rheological properties of fractionated PFPEs with different molecular weights and endgroup functionalities (Fomblin Z, Zdol, and ZdolTX) at various temperatures. From the study of melt viscosity *vs.* molecular weight (M), we observed a remarkable crossover at a critical M for ZdolTX while not for Zdol, which may be due to the peculiar coupling of strongly functional endgroups. The temperature dependence on viscosity was further examined via the Arrhenius equation, where the activation energy for PFPE was found to be weakly dependent on M , but increased drastically with the endgroup functionality strength. The complex shear modulus, $G^* = G' + iG''$ (G' : storage modulus and G'' : loss modulus) as well as the modified Cole-Cole plot (G' *vs.* G'' plot) were also examined. G'' is found to be strongly dependent on temperature, exhibiting different microstructures at various temperatures.

The measured bulk rheological properties as well as nano/micro-rheological characteristics were first investigated via equilibrium molecular dynamics simulations. Clusters of chain-ends were typically observed for functional PFPE bulk, which is responsible for the peculiar rheological response measured. Further, by integrating the so-called SOLLD equation of motion and imposing the Lee-Edwards' boundary condition [3], non-equilibrium molecular dynamics simulations of static and oscillatory PFPE bulk shearing were realized with a constant temperature. By calculating the off-diagonal component of film stress tensor, viscosity and G^* were extracted as functions of molecular architecture (*e.g.*, M and endgroup functionality) and external conditions (*e.g.*, temperature and pressure), where a critical temperature exists to overcome the activation energy barrier and modify the PFPE melt structure. Both the discrete and continuous relaxation time spectra were also estimated, which has shown a broader distribution for strongly functional PFPEs. Different relaxation models, including Maxwell, Cole-Cole, Cole-Davidson, and Havriliak-Negami models, were incorporated and compared with our simulated G^* data. We found that Cole-Cole model fits our preliminary results best.

Since the confinement of molecules in dimensions comparable to their size gives rise to a unique behavior, we are currently generalizing our work to incorporate the nano/micro-scale confinement effect, which provides a full scale modeling capability for PFPE lubricants.

[Reference]

1. Jhon, M.S., "Physicochemical Properties of Nano Structured Perfluoropolyether Films", *Advances in Chemical Physics*, 129 (2004), 1-79.
2. Karis, T.E. and Jhon, M.S., "The Relationship between PFPE Molecular Rheology and Tribology", *Tribology Letters*, 5(1998), 283-286.
3. Allen, M.P. and Tildesley, D.J.; *Computer Simulation of Liquids*; Oxford Science Publications; ISBN 0198556454.