Final Project Report for Grant: DE-FG02-07ER46455

Grantee: Cornell University; **Project Title:** Tethered Lubricants

Principal Investigator: Lynden A. Archer

Performance Period: 07/01/2007-09/15/2010

Accomplishments

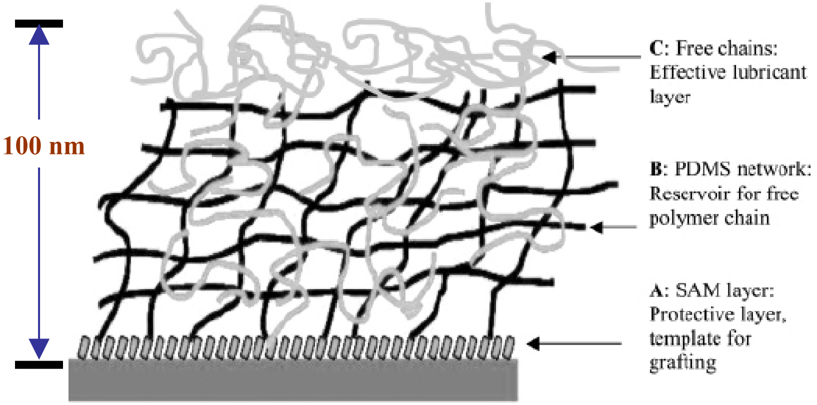

Fig. 1 Schematic of tethered, three-tiered thin film lubricant.

Under DOE support (DE-FG02-07ER46455 & DE-FG02-02ER46007), we have performed extensive experimental and theoretical studies of interfacial friction, relaxation dynamics, and thermodynamics of polymer chains tethered to points, planes, and particles.[1-24] A key result from our tribology studies using lateral force microscopy (LFM) measurements of polydisperse brushes of linear and branched chains densely grafted to planar substrates is that exceedingly low friction coefficients $\mu \approx 4 \times 10^{-3}$, i.e. comparable to an ice-skater on ice, for these systems.[6-9] These friction coefficients are among the lowest values reported;[25] and are certainly the lowest recorded for a dry polymer brush. Our observations have been rationalized using an Eyring-type model for friction of a viscoelastic brush,[1-9] and within this framework can be understood in terms of the inherently low interfacial shear stress of the polymers studied (e.g. polydimethyl siloxane, PDMS)[7-9] and the larger interfacial stress activation volume and higher surface mobilities of tethered polymers comprised of a preponderance of chain ends.[13-15,26-29]

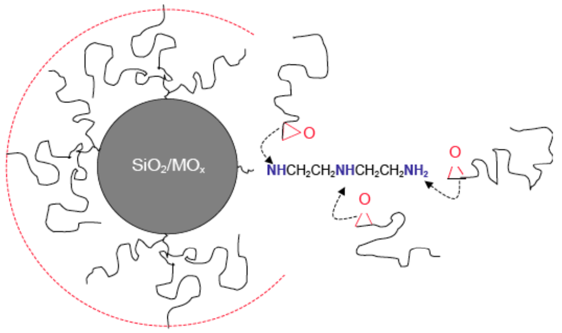

Fig. 2 NOHMs based on covalent epoxy-amine linkages.

Specific project achievements include: (1) Synthesis of three-tiered lubricant films containing controlled amounts of free and pendent PDMS chains, and investigated the effect of their molecular weight and volume fraction on interfacial friction.

(2.) Detailed studies of a family of hairy particles termed nanoscale organic hybrid materials (NOHMs) and demonstration of their use as lubricants. In particular, NOHMs comprised of PDMS/PEG chains (corona) tethered to the surface of inorganic nanostructures (Figure 2) show unusual rheological and tribological features We have characterized the bulk rheology of these materials and discovered several novel behaviors, including time-strain superposition, which allows one to interrogate dynamical properties on extraordinarily long timescales of 10^{23} s (ie. 10^{15} years) from a one-day experiment. Significantly, NOHMs lubricants based on PEG-like corona have been found to be completely biodegradable and hold excellent promise as bulk lubricants for marine craft. Working in collaboration with a local company, Summit Lubricants, we have characterized the wear, additives tolerance, thermal, and tribological properties of PEG-based NOHMs lubricants using a suite of

ASTM standardized tests. Results from these tests indicate that multiple hairy nanoparticle onfigurations are promising for large-scale trials.

A. Tethered Lubricants.

During the first year of this project, we reported that multi-tiered, thin-film lubricants comprised of a dense SAM under-layer and a hyperbranched, polydimethyl siloxane (PDMS) corona (Fig. 3) manifest the lowest coefficients of friction COF ever recorded ($\mu \approx 5 \times 10^{-3}$) for a dry lubricant film. These friction coefficients are comparable to those experienced by an ice-skater on ice or measured in the knee joint of rabbit animal models; both situations where low molar mass liquids (melted water and synovial fluids, respectively) are believed to play a role in lubrication. That comparably low levels of friction can be achieved in a dry, tethered film of nanometer dimensions is a truly remarkable observation. In order to fully take advantage of this effect, it is clear that its fundamental origin must be understood.

Our first hypothesis (see ref 8) was that the branched architecture of the PDMS corona was the source of the ultra-low friction coefficients observed. This led to multi-tiered, micron-sized, tethered coatings comprised of model, end-linked PDMS networks as corona. The only source of branches in these systems is the small amount (typically < 1%) of mono-functional precursor PDMS chains that cannot be fully integrated in the network and are thus best viewed as end-linked pendent chains randomly distributed in the corona. To understand the effect such chains might have on the COF, we deliberately seeded our networks with mono-functional PDMS precursor chains of well defined molecular weight, allowing both the number density (volume fraction of the precursors) and molecular weight of the pendent chains to be facilely adjusted and its effect on interfacial friction quantified.

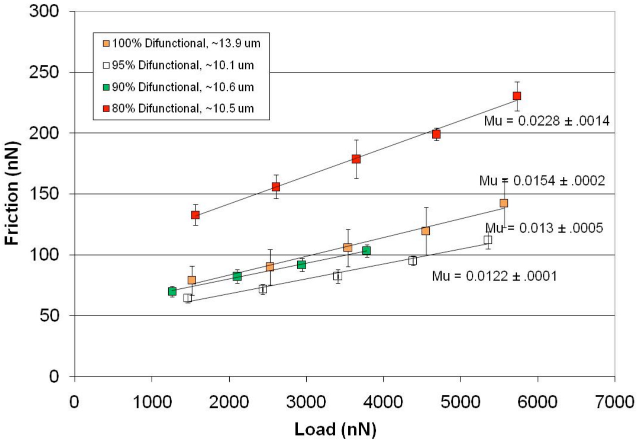

Fig. 4 Friction force versus normal load for 9.4 k PDMs networks containing varying concentrations of 8.9K PDMS pendent chains.

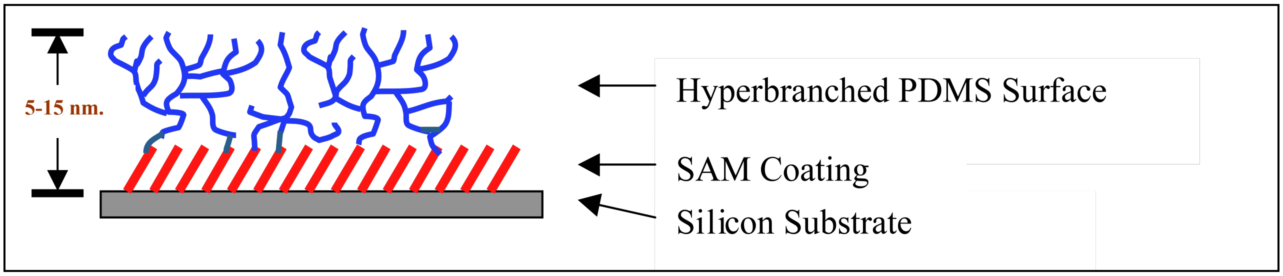

Fig. 3 Schematic of hyperbranched thin-film tethered lubricant coatings.

Figure 4 compares the COF obtained using PDMS corona based on a difunctional precursor M_w = 9, 400 g/mol and monofunctional PDMS additive (M_w = 8,900 g/mol) of approximately the same molecular weight. By varying the volume fraction of the additive in the blend prior to cross-linking, it is possible to systematically adjust the composition of pendent chains in the lubricant corona. It is apparent from the plot that while all of the PDMS-SAM films manifest rather low friction coefficients, networks prepared using the highest volume fraction of mono-functional chains manifest the highest COF values. A PDMS network containing 20% pendent chains is so poorly formed that it is for all practical purposed comparable to the randomly branched corona hypothesized as the cause of the ultra-low COF values in our earlier experiments. That Figure 4 shows networks with the largest fraction of pendent chains manifest the highest COF values, is clearly at odds with the hypothesis that the hyper-branched architecture of the thin network films is the source of the ultra-low friction coefficients observed. Figure 5 indicates that pendent chains can however significantly lower interfacial friction at high sliding rates. Specifically, this figure shows that while at low sliding rates pendent chains increase the COF and hence friction force, pendent chains weaken the slope of the *F* versus *V* curve and delays the onset of ware (this coincides with the upturn seen in *F* at high sliding speeds). Thus at high sliding velocities, the more branched loosely formed structure of PDMS corona hosting numerous pendent chains manifest the weakest increases in friction force with sliding speed.

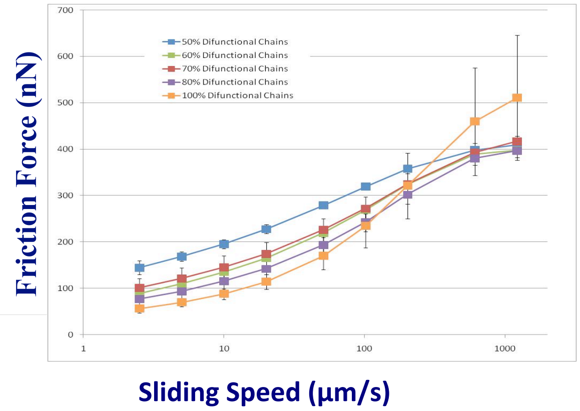

Fig. 5 Friction force versus sliding speed for 9.4K PDMS networks containing variable amounts of 8.9K PDMS dangling/pendent chains.

A simple variation of our scheme for introducing pendent chains into the PDMS corona can be employed to add free chains. Although this configuration provides no obvious benefits for understanding the underlying causes of the frictional properties of thin PDMS films, it provides the exciting possibility of creating tethered lubricants that encapsulate a mobile component that might, for example, be harnessed to heal regions of the coating damaged by wear. Specifically, by blending controlled amounts of non-functional PDMS with any desired molecular weight into the di-functional precursor, it is possible to tethered networks with well defined geometries and strand lengths, which serve as host for mobile, guest polymer chains of the same chemistry and possessing any desired molecular weight. Figure 6 summarizes our preliminary results probing the effect of such guest chains on the COF of tethered PDMS coatings. In this case the molecular weight and volume fraction of the difunction PDMS precursor chains are fixed at M_w = 28,000 g/mol and ϕ = 0.9, respectively. Surprisingly, we find that the lowest COFs are seen at intermediate ($M_{w,free} \approx$ 6,000 g/mol) molecular weights. The origin of this behavior is currently not known, but is still under active investigation. We suspect, however, that it reflects the balance between mechanical reinforcement to the coatings provided by larger, entangled ($M_{e,PDMS} \approx$ 8,100 g/mol), and the greater surface activity and lower viscosity of lower molecular weight guests. The former effect lowers the friction coefficient by reducing the area of contact between the probe and substrate, the latter lowers it by reducing viscous dissipation at the interface. Through a combination of experiment and theory, we will decouple the two effects and determine what role they play in our observations.

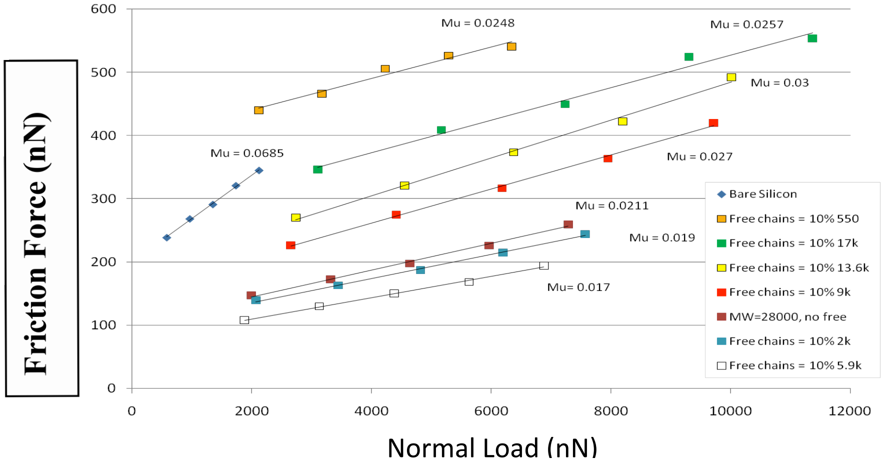

Fig. 6 Friction force versus normal load for 28K PDMS networks swollen with 10 vol% mobile PDMS chains with varying molecular weights.

B. Organic-Inorganic Hybrid Lubricants

In the previous progress report we outlined a new class of nanoscale organic hybrid materials (NOHMs, Fig. 7) discovered in our group. We also discussed potential

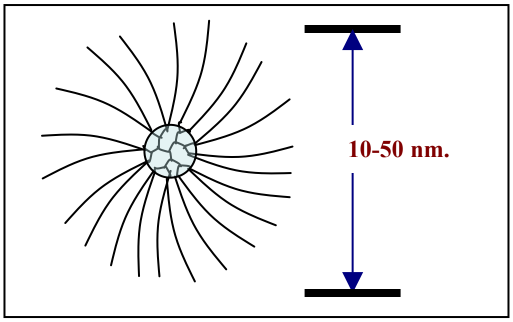

Fig. 7 Schematic building-block for nanoscale hybrid lubricants

applications of these fluids as lubricants. During the last year we filed a broad invention disclosure covering these materials and have demonstrated their practical benefits as bulk lubricants and electrolytes for next-generation rechargeable, lithium metal batteries.[3]

Our work under DOE support focuses on using NOHMs as platforms for both scientific and applications-oriented studies. To date we have focused on a family of NOHMs based on SiO_2 nanoparticle cores and polyethylene glycol (PEG) corona. These materials are facilely synthesized and their physical properties readily manipulated by varying the core particle size, mass distribution (e.g. filled or hollow) and the PEG molecular weight, grafting density and polydispersity. Figure 8, for example, illustrates the effect of corona grafting density on fluid flow properties. The figure shows that for a fixed corona molecular weight, $M_{w,PEG}$ = 700 and SiO_2 diameter, d_{SiO2} = 10nm., it is possible to create materials that completely flow under gravity (rightmost vial) to ones that have a yield stress substantially greater than the gravity stress (leftmost vial), and as such do not flow at all. Materials in the last group are interesting for at least two reasons:

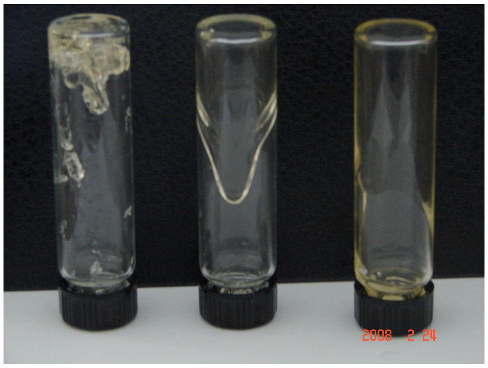

Fig. 8 Liquid NOHMs based on PEG corona and 10 nm. diameter SiO_2 cores. The volume fraction of the core particles increases from right to left in the figure.

(i) They manifest unusual rheological properties. One of the most useful aspects of this is already demonstrated in Figure 8, where their facile tunability is illustrated. Easily the most striking aspect is illustrated in Figs 9(a) –(c), where the dynamic rheology, G' and G'', of a single NOHMs material is reported for a single temperature, fixed range of mechanical frequencies ω, at varying shear strains γ (Fig a). Figure (b) shows that mechanical data obtained at discrete shear strains can be superposed to produce a single "master" curve spanning more than 23 decades in frequency. The facility demonstrated in these figures wherewith modest shear strains can be employed to probe the extremely distant future of a materials transient behavior was heretofore unknown. Additionally, Figure 9(c) shows that the so-called horizontal shift factor a_T needed for the superposition is a universal function of strain identical in form to the WLF equation (solid line through the data) well-known in the polymer

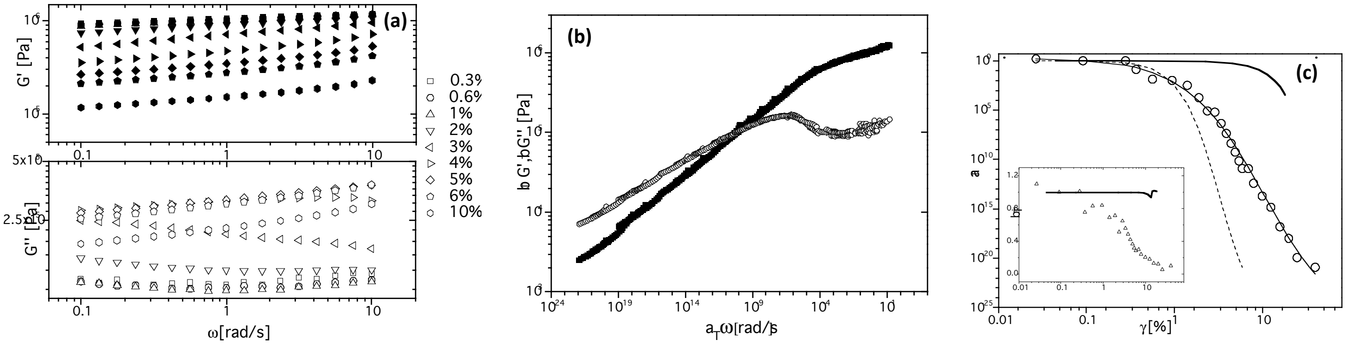

Fig. 9 (a) Frequency-dependent viscoelastic storage G' and loss G'' moduli for NOHMs liquids at T = 60 °C and shear strains ranging from 0.3% to 10%. **(b)** Viscoelastic "master" curves obtained from horizontal and vertical shifting with respect to a reference strain in the linear viscoelastic flow regime; **(c)** Horizontal, shift factor a_T required to achieve superposition plotted as a function of shear strain, γ. The line through the data is a prediction based on a WLF-like analysis. The other lines that do not agree with the experimental a_T are obtained using two other theories.

science literature, with shear strain replaced by temperature. Our findings indicate that in NOHMs fluids the shear strain plays the same role as temperature in simple polymers, which is consistent, at least qualitatively, with expectations for soft glasses. It must be emphasized, however, that this agreement is only qualitative because the strain dependent a_T values predicted using the soft-glassy rheology (SGR), model (Fig 9(c), upper dark line), are in uniform disagreement with our experimental observations.

(ii) PEG NOHMs fulfill a substantial, unmet need for biodegradable lubricants. These lubricants are important for large naval vessels and machinery because they can be safely disposed of at sea. This is argued to producing improvements in fuel economy because spent lubricating oils and greases do not need to be transported to ports for disposal.

During the last year of the project, we have worked with a local company, Summit Lubricants, to characterize the interfacial friction and wear characteristics of several NOHMs lubricant designs. This effort has led to several candidate materials that display lubrication properties comparable to their non-degradable counterparts. Furthermore, because the lubricating molecules are chemically tethered to a nanoparticle, loss of the lubricant by evaporation is eliminated, facilitating high-temperature and generally difficult vacuum applications. Our initial results indicate that the viscous flow properties of NOHMs can be tuned over a broad range by varying the molecular weight and grafting density of the corona species. For oligomeric PDMS corona densely tethered to silica nanostructures, the materials are neat liquids (Fig. 6(a)) with viscosities spanning the spectrum from simple Newtonian liquids to yield stress solids. We have found that NOHMs that manifest a yield stress generally possess shear-independent and weakly temperature-dependent viscoelastic properties, both highly desirable features for a lubricant.

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