

# Modeling Molecular Structure to Tribological Performance

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## ABSTRACT

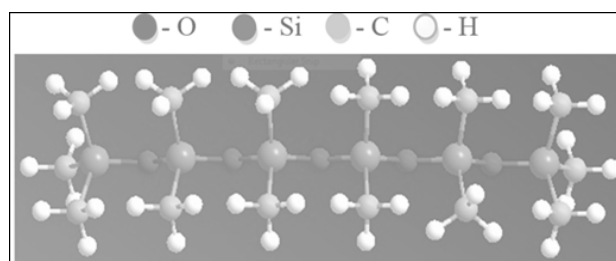
When designing and employing lubricants, film thickness modeling techniques must be used as part of an overall design approach to ensure mating components, in relative motion, have proper lubricating films to separate surface asperities. Improper asperity separation will lead to increased friction and wear, and overall reduction in system reliability, serviceability and efficiency. Many of the tools used today to model tribofilms are rooted in empirical studies completed with hydrocarbon-based fluids as the lubricating medium. Generally, these modeling techniques have also been applied to non-hydrocarbon-based lubricants, but this may not be an accurate method to model such fluids. As demands for improved lubricant performance continue to rise, so too does the need for improved tribofilms modeling techniques. This paper will discuss a modeling technique developed in which silicone-based polymer molecular structures are designed with tribological film performance in mind. The models consider molecular structures of various traditional and newly developed silicone fluids and relate that structure to rheological performance. Expected rheological

performance is then used to model tribological film formation and characteristics. The output of these tribological film formation and characteristic models can then be fed back to the molecular structure module and iterated to achieve optimal molecular structure for the intended tribological performance. In addition, a graphical user interface has also been developed to aid in the data input to the modeling software.

## INTRODUCTION

Polysiloxanes, or silicones, are available in a wide variety of molecular structures that feature the Si-O-Si backbone. The synthesis and manufacturing process is complex, starting from the reduction of quartz, a continuous crystalline structure of  $\text{SiO}_4$ , to elemental silicon. Then, using a fluid bed reaction process, silicon and methyl chloride form various chlorosilanes with the majority constituent being dichlorodimethylsilane. These chlorosilanes are distilled and hydrolyzed, and subsequent polymerization results in polysiloxanes. The siloxanes are then further processed to attach hydrocarbon functional groups to the Si-O-Si backbone, giving rise to a

**Figure 1: Structure of Polydimethylsiloxane (PDMS)**



myriad of different siloxane types. The most basic of these is polydimethylsiloxane (PDMS), shown in Figure 1, which has a  $\text{CH}_3$  Methyl functional group connected to the Si-O-Si backbone.

The Si-O bonds of siloxanes are > 30% stronger than C-C bonds of hydrocarbons, giving the molecules great stability. Additionally, the Si-O-Si bond angle is about 24% larger than the C-C-C bond angle found in hydrocarbons. This allows siloxane molecules to have great flexibility. The strength, length, and flexibility of silicone bonds impart many unique properties, including low melting temperature, fluidity, low glass transition temperature and increased compactness. With these properties siloxanes can be used in many diverse applications in different industries. As a lubricating base fluid, the exceptional oxidative stability and temperature-viscosity indices stand out versus other

**Table 1: Load, oxidation stability and viscosity index of various siloxanes and other synthetic fluids**

	SRV ok load (N)	4-ball scar (mm) 400 N/hr	DSC, OOT	Visc. -35°C	Visc. 40°C	Visc. 100°C	VI
PAO-6	350	0.822	202	3424	26	5.6	163
PDMS	300	SEVERE	286	234	35	16	466
PDMS, Formulated	975	1.378	221	141	22	9.7	473
Dimethyl+hexyl	2,000	0.879	204	X	28	8.3	298
PFPE-Y Branched	2,000	0.727	500	54,450	94	15.1	169
Trifluoropropyl	550	1.182	246	36,386	159	29.6	228
PFPE-Z Linear	600	1.485	500	3,591	160	46.3	332

synthetic lubricant base fluids such as Polyalphaolefins, Polyalkyleneglycols, Polyol- or Dibasic-Esters, and in some ways even rival perfluoropolyethers.

### TRADITIONAL SILOXANE VARIETIES

Despite high viscosity index, oxidative stability and strong bond strength, the large bond angle spacing of the siloxane molecule renders them very compressible compared to hydrocarbons and other synthetics; subsequently, making them relatively poor lubricants. With this in mind, siloxane variations incorporating higher amounts of

hydrocarbon functionality have been on the market since the 1950s. In addition to methyl functional groups, phenyl, heptyl, and octyl groups have been attached to the siloxane backbone. The intent is to bring about more hydrocarbon lubricant type behavior, while still enjoying the aforementioned properties of the Si-O-Si backbone. For example, phenylmethyl siloxanes (PMS) have higher onset oxidation temperatures and carry load better than PDMS. However, they also have lower viscosity indices. In the 1970s, fluoro-functional siloxanes were introduced to bring about better load carrying capacity. In achieving

load carrying characteristics, however, onset oxidation temperature and viscosity index was reduced relative to PDMS and PMS. Table 1 shows some relative differences of various siloxanes and other synthetic fluids.

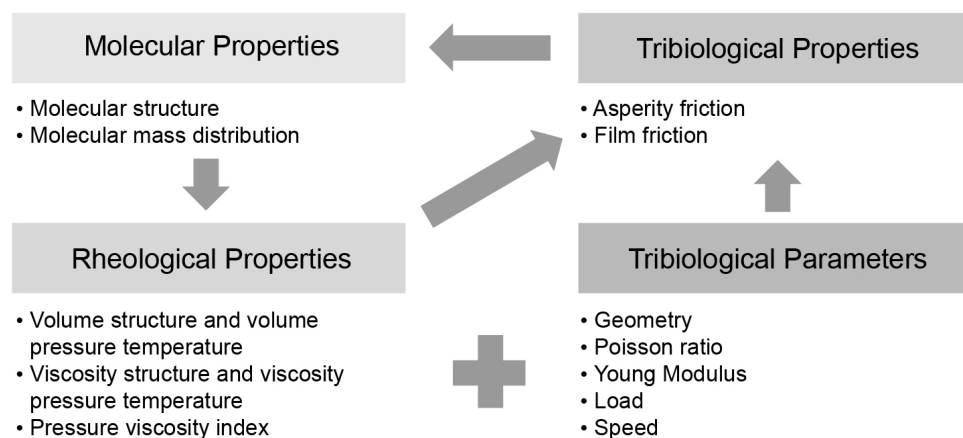
As can be seen, thermal and oxidative properties of siloxanes are still among the highest available, but load carrying remains an area for improvement. With this in mind, new siloxane developments aim to improve load carrying even further. To do this, it is imperative to understand the impact molecular structure has on not only thermal and oxidative stability, but more importantly the impact on tribological performance.

### MODEL-BASED SILOXANE STRUCTURE DESIGN: FROM MOLECULE TO TRIBOLOGY

Recently MOLYKOTE®, in cooperation with Northwestern University, developed a modeling system for designing future siloxane structures with excellent lubricity characteristics, such as high load carrying capacity and strong film formation capability. The objective was to identify the relationship between molecular structure and rheological/tribological properties to find structures with superior lubricity characteristics. Figure 2 shows the conceptual approach used to create the model.

Initially, the rheological properties using molecular parameters of the structure are determined. Different siloxane structures are investigated for their tribological parameters and properties, and this is fed back to the molecular structure to be optimized through iteration. Molecular structure elements used in the model were: the percentage of functional branch content, Q; the length of alkyl branch (Carbon atoms), L;

**Figure 2: Modeling System: from Molecule to Tribology**



the type of branch (Alkyl, Phenyl, Cyclic, Fluoro),  $J$ ; and the atomic Length (Silicon and Oxygen atoms),  $Z$ ; of the polymer. Figure 3 shows the structure elements and equations used to calculate rheological properties: specific volume, viscosity and pressure-viscosity coefficient. Knowing molecular structure, molecular weight and Van der Waals volume ( $v_w$ ), it can be easily calculated. The Molecular Packing Factor is the quotient of Specific Van der Waals Volume over measured Specific Volume ( $v_0$ ). The Specific Volume at room temperature and atmospheric pressure ( $v_0$ ) can be calculated using Molecular Packing Factor.

The viscosity ( $\eta_0$ ) can be calculated using the structure-viscosity equation of Berry and Fox which includes the parameters of Radius of Gyration and Monomeric Friction, which is described on the right side of Figure 3. The outcome is the Tait equation of state ( $v(T, P)$ ) which best describes the pressure and temperature dependence of the Specific Volume, and the Tait Doolittle equation ( $\eta(T, P)$ ) which is used to calculate the temperature and pressure dependence of viscosity. During the experiment partial film

thickness and film friction were measured with the PCS EHL instrument. Lubricants were tested using a ball-on-disk machine to determine the effects of molecular structure on boundary friction and wear. Total Friction is the summary of two components: asperity and film friction. In hydrodynamic lubrication, viscosity alone determines the coefficient of friction and film thickness. In elastohydrodynamic lubrication, friction and film formation are decoupled and three properties become influential in the optimization of lubricants: the viscosity at atmospheric pressure, the pressure-viscosity index influence on overall film formation and the limitation of shear stress on the elastohydrodynamic friction coefficient.

In order to manage all of the inputs and outputs to the model, a Graphical User Interface (GUI) was constructed. Figure 4 shows the GUI that was developed using the experimental data and equations from the literature. Polydimethylsiloxane (PDMS) is the basis for the model with options to choose the following branch structures:

- Alkyl (PAMS)
- Fluoro (PFMS)

- Cyclohexyl (PCMS)
- Phenyl (PPMS)

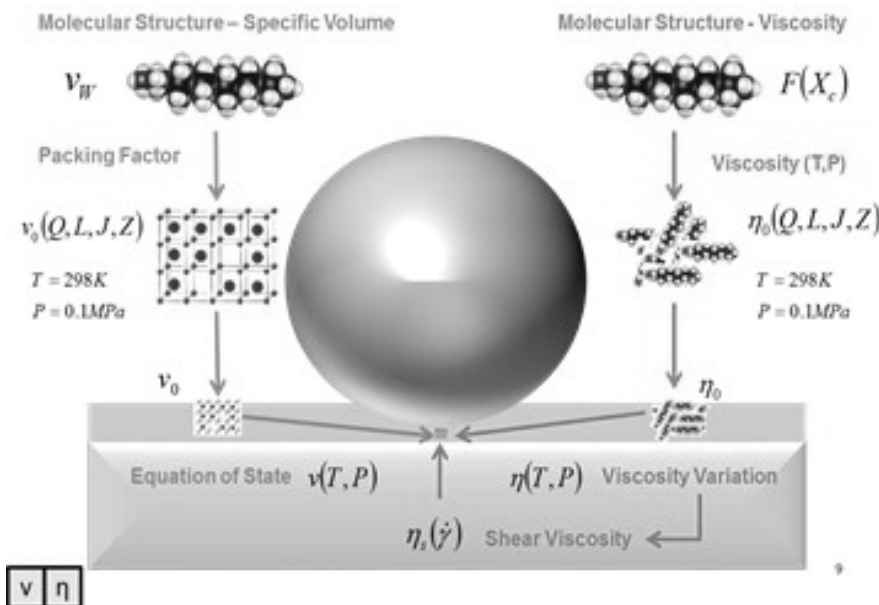
Input variables are:

- Temperature
- Branch length (for Alkyl)
- Polydispersity
- Load
- Branch content percentage
- Polymer length
- Speed
- Slide-roll ratio

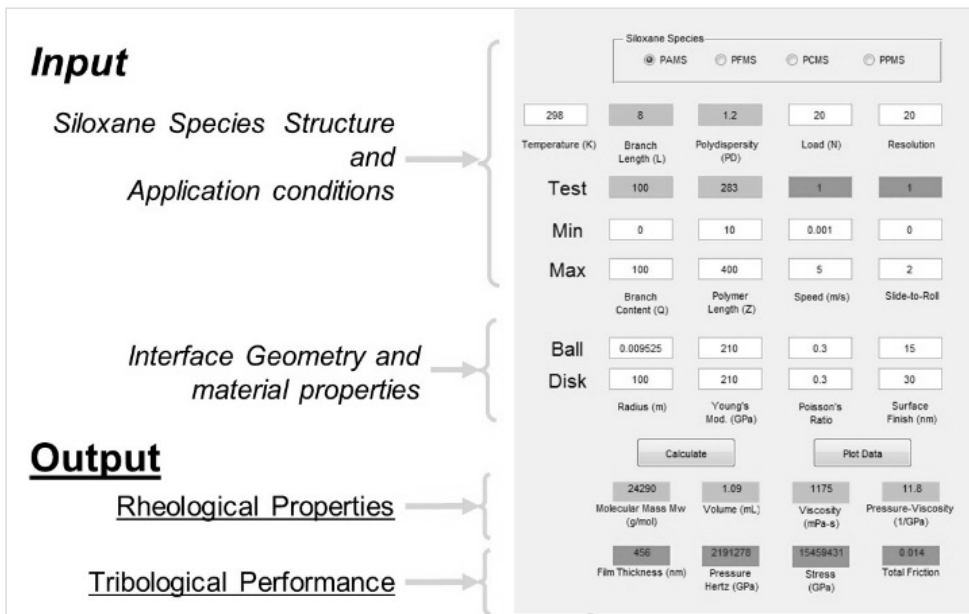
Ball and disk characteristics are also inputs to the model (disk is set at 100 to simulate infinite flat surface).

- Diameter
- Young's modulus
- Poisson ratios
- Surface finish

**Figure 3: Modeling system: from Molecular to Rheological**



**Figure 4: Graphical User Interface**



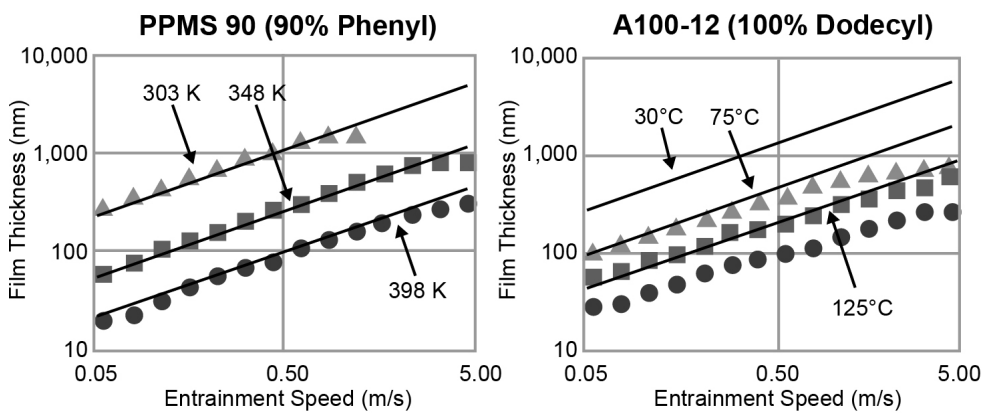
The output data is contained in the last two rows. Molecular mass, volume, viscosity and pressure-viscosity are the molecular-to-rheological transformation data. Film thickness, Hertzian pressure, stress and total friction are the rheological to tribological transformation data.

## RESULTS

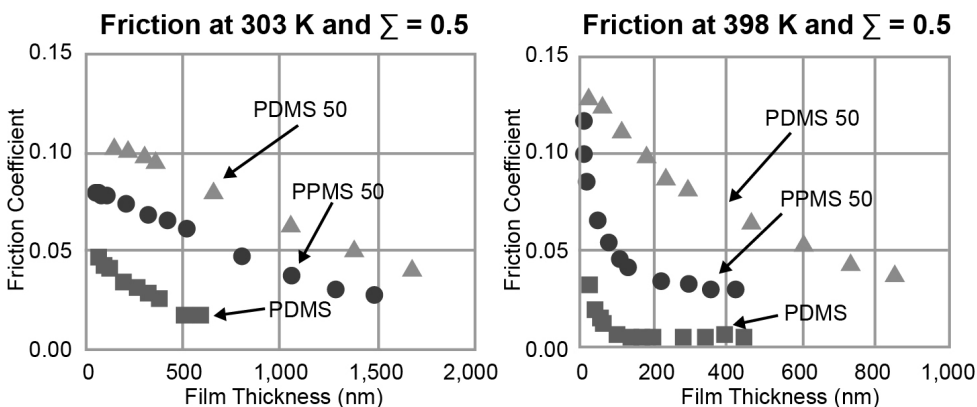
Figure 5 shows two Film Thickness to Entrainment Speed graphs for phenylfunctional siloxane (PPMS 90) and alkylfunctional siloxane (A100-12) at different temperatures. Ring structured branches (aryl PPMS) show nearly Newtonian behavior. High monomeric friction allows a relatively low molecular mass ( $M_w = 1990$  g/mol for PPMS 90) to build viscosity, so shear thinning is low. On the right side of Figure 5 we can see different behavior for alkylfunctional fluids. Low monomeric friction requires a relatively high molecular mass ( $M_w = 29900$  g/mol for A100-12) to build viscosity, so shear thinning is high. Linear branches may exhibit temporary shear-thinning. Figure 6 shows the coefficient of friction versus film thickness for three different structures: polycyclohexylmethylsiloxane (PCMS 50), polyphenylmethylsiloxane (PPMS 50) and standard polydimethylsiloxane (PDMS) at two temperatures. For PCMS, the CoF does not change much with temperature. In the case of PPMS and PDMS, CoF drops at higher temperatures. This indicates that Cyclohexyl siloxanes has greater thermal stability in the fluid film region.

Generally speaking, it is seen from these examples that siloxanes can be adapted to diverse application, for example, cycloalkylsiloxanes could be used as traction fluids or alkylsiloxanes as energy efficiency lubricants.

**Figure 5: Newtonian and Non-Newtonian Siloxanes**



**Figure 6: EHD Friction for Cyclic Branched Silicones**



## APPLICATIONS

Polydimethylsiloxane-based greases and compounds find use as O-ring and valve lubricants, damping grease, plastic gear lubricants or brake caliper greases. Phenyl siloxane molecules provide additional thermal and oxidation resistance but do not improve lubricity. Polyphenylmethylsiloxane-based greases are used in metal-to-metal applications requiring high temperatures, such as clutch release bearings or overrunning clutches that require slip prevention. Trifluoropropyl siloxanes exhibit reasonable wear protection and load carrying capacity, though oxidation stability is not as good as the Phenyl siloxanes. Typical applications of polytrifluoropropylmethylsiloxanes are for pumps, mixers or valves in the chemical industry and circuit breakers. Ph/F copolymer-based greases thickened with PTFE show good results (as shown in Table 6) at high temperatures (220°C) in FE 9 bearing application tests. Based on this characteristic, bearings running at high and/or broad temperature ranges might be an interesting application for this kind of grease.

## OUTLOOK

Newly synthesized temporary shear thinning Polyalkylmethylsiloxanes, high traction Polycyclohexylmethylsiloxanes and the high temperature Ph/F copolymer Siloxanes are examples for the tribological potential of siloxanes beyond the specialty use of Polydimethylsiloxanes, Polyphenylmethylsiloxanes and Polytrifluoropropylmethylsiloxanes. Modeling tools can be used to optimize the chemical structure for a specific tribological need, and tailored siloxane fluids for specific tribological challenges as described above. The researcher could extend modeling techniques to other types

of chemical structures besides silicones, explore the impact of mixtures and additives to the model or introduce functional groups (S, N, P) to the side groups. Ph/F siloxane copolymer greases are defining a new class of lubricating siloxane fluids which solve some limitations of the currently used polysiloxanes. The flexible structure defined by the ratio of Phenyl and Fluoro functional groups allows the design of specific fluids at high thermal stability and improved wear resistance. The good solubility of commercially available additives allows the recreation of lubricants for a broad range of applications.

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