Development of High-Service-Temperature Fluids

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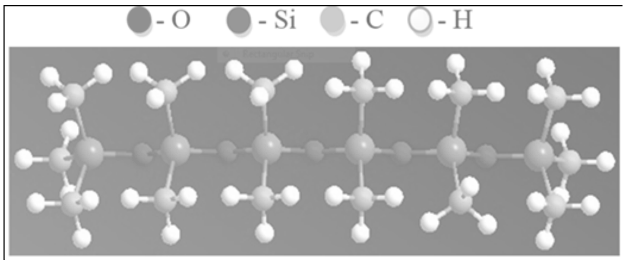
ABSTRACT

Silicone fluids are known to have high Viscosity Indices (VI), and high Oxidation Onset Temperatures (OOT). Silicone VI and OOT characteristics make these fluids appealing for use as lubricants in high temperature applications, and where lubricant longevity is desired. Despite thermal and oxidative benefits, silicones lubricants have a reputation as being poor lubricants in metal-to-metal applications and are typically only selected for use in plastic applications. Most industrial knowledge about silicone lubricants is based on characteristics of PolyDi-Methyl Siloxanes (PDMS), in which case, lubricity limitations do exist. However, there are other silicone-based lubricating fluid technologies, that have been commercially available for decades, that far exceed known lubricity performance of PDMS, and in some ways, can rival traditional synthetic hydrocarbon. Phenyl-Methyl Silicones (PMS), Fluoro-Silicones (FS), and Alkyl-Methyl Silicones (AMS) can offer great performance at high temperatures due to the high VI and OOT for which silicones are known, and their molecular structures enable improved lubricity as compared to PDMS, giving these unique silicones combinatory benefits of thermal and oxidative stability and lubricity, even in metal-to-metal applications. This paper will discuss and compare different silicone-based fluids, as well as some comparison to polyalphaolefins, perfluoropolyethers, and other common synthetic lubricant technologies. Basic molecular structures will be reviewed, and comparative test data will be shared, including SRV Schwingungs-Reibungs und Verschleisstest) data, 4-Ball wear scar data, Viscosity Index and Differential Scanning Calorimetry (DSC). Following data sharing, a few potential high temperature applications ideas will be presented.

Figure 1: Structure of Polydimethylsiloxane (PDMS)



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 SiO_4, to elemental silicon. 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 myriad of different siloxane types. The most basic of these is polydimethylsiloxane (PDMS), shown in Figure 1, which has a 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 synthetic lubricant base fluids, such as Polyalphaolefins, Polyalkyleneglycols, Polyol- or Dibasic-Esters, and in some ways, even rival perfluoropolyethers.

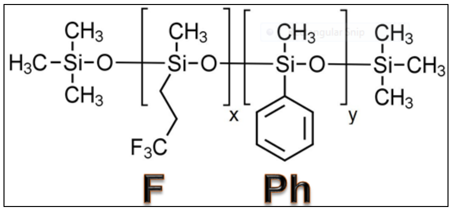
TRADITIONAL SILOXANE VARIETIES

Despite high viscosity index, oxidative stability and strong bond strength, the large bond angle spacing of the siloxane molecule renders them very compressible as 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, hectyl 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 were 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.

PHENYL-/FLUORO-SILOXANE COPOLYMER LUBRICANTS

The chemistry of siloxanes is diversified. The most common siloxane structure is polydimethylsiloxane which finds application in lubricants as well but it has limited wear resistance. Phenyl functional groups provide additional thermal and oxidative resistance but do not necessarily improve lubricity. Trifluoropropyl siloxanes exhibit reasonable wear protection and load carrying capacity, however their oxidative stability is not as good as Phenyl siloxanes. Copolymerization technology allows different siloxane monomers with specific properties to be copolymerized into a single molecule. The subsequent, new fluids exhibit properties of both siloxane monomers included in the copolymer. The balance of monomer ratio allows the development of specific properties and the degree of polymerization is used to make copolymers in a broad range of viscosity. This technology is used to develop copolymers containing Phenylmethyl siloxanes and Trifluoropropylmethylsiloxane. These Phenyl-/Fluoro-copolymers (Ph/F copolymers) combine the excellent temperature stability of Polyphenylmethylsiloxane with the enhanced wear resistance properties of Polytrifluoropropylmethylsiloxanes.

Figure 2: Structure of Ph/F copolymer fluid



Considering the modeling nomenclature from above, Z is the sum of x and y repeating units, Q is the percent copolymer (the remaining balance being methyl), and J presents the two types of branching.

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

PROPERTIES OF PH/F COPOLYMER NEAT FLUIDS

Thermal stability of three different fluoro-to-phenyl ratios has been determined by thermally treating with both open and closed cup at 250°C and then measuring viscosity weekly.

Figure 3: Thermal stability of copolymer fluids

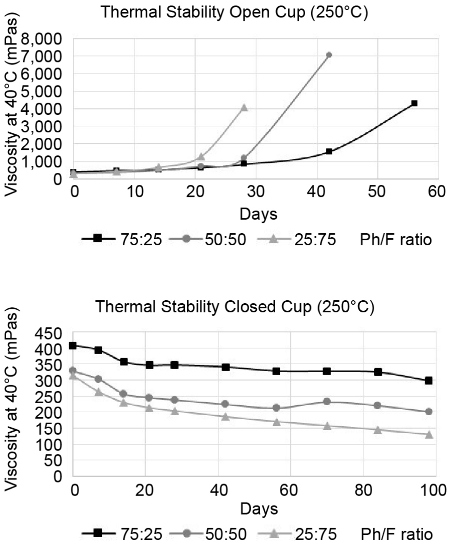


Figure 3 shows that the viscosity of Ph/F copolymers is stable over a period of more than 20 days when stored in open cups. Copolymers with higher phenyl content (75:25) demonstrate a better thermal stability than those with higher fluoro content (25:75). In closed cups where no evaporation occurs, the viscosity is stable over a period of more than 100 days. Table 2 shows the thermal stability of copolymer fluids compared to other lubricating fluids.

Table 2: Comparison of Ph/F copolymer fluids with typical lubricating fluids

Fluid	Ph/F 75:25	Ph/F 50:50	Ph/F 25:75	PAO	POE	PMPS	FS	PFPE (branched)	PFPE (linear)
VI	229	239	242	155	145	220	241	108	338
TGA* (250°C)	98.6%	99.0%	99.0%	97.4%	96.5%	99.1%	97.2%	93.4%	99.3%
DSC**	282°C	283°C	277°C	205°C	203°C	366°C	246°C	348°C	330°C
Evap*** (200°C, 7 days)	0.13%	0.47%	0.65%	7.85%	13.38%	1.46%	18.50%	Not tested	Not tested

* TGA: 30-500°C, 10°/min, Air 60 ml/min

** DSC: 30-500°C, 10°C/min, Air 60 ml/min

*** internal test method

Ph/F copolymer fluids show viscosity indices (VI) of about 230-240, similar to highly phenylated and fluorinated siloxane fluids. Compared to other lubricating fluids, these values are higher than most hydrocarbon and branched PFPE fluids. Some additional comparisons have been made by using thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). Both methods indicate superior thermal stability of Ph/F copolymers compared to PAO, polyolester and fluorosiloxane fluids. Table 3 shows wear resistance data in accordance with DIN 51350-3. Wear scar average of the three steel balls after applying a load of 400 N and 800 N for 1-hour test duration are reported. While no data could be generated for phenylmethylsiloxane fluid (based on the high load), wear scars for all three investigated copolymer ratios were obtainable. The results confirm the assumption that copolymer fluids with higher fluoro content have smaller wear scars.

Table 3: Wear resistance of neat copolymer fluids

Fluid	Ph/F ratio	400 N load	800 N load
		average wear scar diameter	
	75:25	1.53 mm	Not measurable
Ph/F copolymer fluid	50:50	1.48 mm	2.82 mm
	25:75	0.55 mm	1.81 mm
Polyphenylmethylsiloxane		Not measurable	Not measurable
Polytrifluoropropylmethylsiloxane		1.18 mm	1.17 mm

Table 4: SRV measurement results (DIN 51834-4, T = 50°C, Freq. = 50 Hz, Load = 300 N, Stroke = 2 mm)

Fluid	Ph/F Ratio	μ (f15)	μ (f30)	μ (f90)	μ (f120)
Ph/F copolymer fluid	75:25	0.129	0.128	0.126	0.125
	50:50	0.128	0.128	0.119	0.118
	25:75	0.121	0.118	0.112	0.111
Polytrifluoropropylmethylsiloxane	ref	0.109	0.104	0.098	0.096
Polyphenylmethylsiloxane	ref	Not measurable			

In addition, wear resistance, as well as coefficient of friction (CoF), on the SRV test machine according to DIN 51834-4 was completed and compared to polyphenylmethylsiloxane and polytrifluoropropylmethylsiloxane fluids.

Table 4 lists the CoF after 15, 30, 90 and 120-minute operating times. These results demonstrate that copolymer fluid CoFs are slightly higher than those of polytrifluoropropylmethylsiloxane fluids.

Compared to polyphenylmethylsiloxane fluids, they show much better results than polyphenylmethylsiloxane at applied loads of 300 N.

PH/F COPOLYMER FLUIDS WITH ADDITIVES

Further investigation of Ph/F copolymers indicate that additive acceptance of this new class of lubricants is much better than with polyphenylmethylsiloxane and polytrifluoropropylmethylsiloxane fluids.

Table 5, for example, shows the improvements in wear resistance (DIN 51350-3) by using commercially available additives compared to the neat copolymer fluid (Ph/F ratio: 50:50).

GREASES WITH PH/F COPOLYMERS

Further focused investigations on the development of greases using Ph/F copolymer fluids have been done as well. These greases can be prepared using single and complex

Table 5: Wear resistance improvements by additives (DIN 51350-3)

Additivation Chemistry	%	400 N load	800 N load
		Average wear scar diameter (change compared to particular neat fluids)	
Antimony o,o-dialkylphoshorodithionate	2.5	0.55 mm (-69%)	1.03 mm (-59%)
Zinc diamyldithiocarbamate	2.5	0.51 mm (-71%)	1.07 mm (-57%)
Dithiocarbamate, ashless	1.0	0.66 mm (-55%)	1.29 mm (-54%)
	2.5	0.62 mm (-58%)	1.16 mm (-59%)
Dialkylpentasulfide	1.0	0.65 mm (-56%)	1.98 mm (-30%)
	2.5	0.82 mm (-45%)	2.07 mm (-27%)
Zinc dialkyldithiophosphate	1.0	0.76 mm (-49%)	1.21 mm (-57%)
	2.5	0.66 mm (-55%)	1.16 mm (-59%)
Amin alkylisooctylphosphate	1.0	1.48 mm (±0%)	1.89 mm (-33%)
	2.5	1.22 mm (-18%)	1.98 mm (-30%)

Table 6: Copolymer grease properties

Characteristic	Test Method	Li-complex Grease	PTFE Grease
Ph/F ratio		50/50	50/50
Base oil viscosity (40°C)		246 cSt	790 cSt
Additives		No additives	No additives
Penetration (unworked/60/10k/100k strokes)	DIN ISO 2137	258/261/282/303	324/not tested
Bleed / Evaporation (24 h/200°C)	ASTM D 6184	0.46%/1.17%	4.58%/0.44%
Dropping point	IP 396-2	340°C	332°C
Flow pressure	DIN 51805	925 mbar (-35°C)	1125 mbar (-40°C)
Emcor corrosion (7 d)	DIN 51802	0	4
Water resistance (3 h, 90°C)	DIN 51807	1	0
DIN 4-ball test (ok load)	DIN 51350	1700 N	1900 N
DIN 4-ball test (wear scar 400 N, 1 h)	DIN 51350	1.05 mm	1.02 mm
FE 9 (F10/F50) (B, 6000 rpm, 1500 N, 220°C)	DIN 51821-2	Not tested	52 h/69 h

soap thickener systems, and also using Polyurea, PTFE and other thickener types. As an example, the results of greases thickened by Li-complex-soaps and PTFE are shown in Table 6.

Ph/F-copolymer greases show excellent high temperature resistance and are suitable in applications where a broad service temperature range is needed. The preparation is similar to that of greases using polydimethylsiloxanes, polyphenylmethylsiloxanes or polytrifluoropropylmethylsiloxanes. Non additized Li-complex greases based on Ph/F copolymer show low bleeding behavior and good corrosion protection at high temperatures. The wear resistance of copolymer greases is much better compared to other siloxane-based grease.

Similar to the neat Ph/F copolymer fluids, the performance can be increased by adding appropriate additives.

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 polytrifluoropropylmethyl-siloxanes 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 creation of lubricants for a broad range of applications.

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