Polyalkylene Glycols

How Different Polymer Architectures Influence Tribology Performance

Martin Greaves
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Objectives

- Show how different polymer architectures of known PAGs can influence rheology and tribology properties.

- Build on our knowledge of PAGs in relation to their rheology and tribology behavior and how an understanding can help us select PAGs with optimum friction control properties.
Contents

- Brief Overview of PAGs
- Chemistry - Polymer Design and Functionality
- EHD Traction Properties and Correlation with Polymer Chemistry
- High Pressure Viscosity Behavior – Pressure Viscosity Coefficients
- Correlating Alpha Values and Traction Coefficients
- Conclusions
Overview of PAG Chemistry

Three key oxide building blocks

- Ethylene oxide
- 1,2-Propylene oxide
- 1,2-Butylene oxide

Traditional synthesis procedure

Initiator (ROH) + Ethylene oxide (EO) +/or Propylene oxide (PO) $\xrightarrow{\text{catalyst} \ \Delta}$ PAG

Initiator plays an important role in determining rheology and tribology behavior. Typically based on alcohols but amines, thiols and other initiators with labile hydrogen atoms can be used.
Established Applications of PAGs
- Air Compressor Fluids
- Natural Gas Compressor Fluids
- Water Glycol Hydraulic Fluids
- Metalworking Fluids
- Quenchants
- Gear Oils

Recent New Applications for PAGs
- Turbine Oils
- Wind Turbine Lubricants
- Non-Sheening Hydraulic Fluids
Conventional Polyalkylene Glycol Technology

**Typical Synthesis Route to Polyalkylene Glycols**

Initiator (ROH) \(+\) \[\text{ethylene oxide (EO)}\] \(+/\text{or}\) \[\text{propylene oxide (PO)}\] \[\xrightarrow{\text{catalyst}}\] PAG

**Types of PAGs by Chemical Family**

- Homo-polymers of EO
- Homo-polymers of PO
- Random copolymers of EO/PO
- Block copolymers of EO/PO
- Reverse block copolymers of EO/PO

PAGs can be designed to a wide range of molecular weights, viscosities and functional performance.

Most common PAG base stocks today.
Monol, Diols, Triols – Different Architectures

Initiator (ROH) + 
\[ \text{ethylene oxide (EO)} \quad \text{propylene oxide (PO)} \]
\[ \text{H}_2\text{C} - \text{CH}_2 \quad \text{H}_2\text{C} - \text{CHCH}_3 \]
\[ \text{catalyst} \quad \Delta \]
\[ \rightarrow \text{PAG} \]

Classical random co-polymers of EO/PO - Impact of Initiator on Polymer Architecture

Monols (“Linear”)

Diols (“Linear”)

Triols (Branched)
Examples of Common PAGs

Monol: PO Homo-polymer

Commonly used in hydraulic, compressor and gear oils

Diol: EO/PO Co-polymer

Commonly used in gear oils, compressors and water based lubricants
Preliminary Traction Measurements

Early experiments conducted 10 years ago using a Mini-Traction Machine on ISOVG-320 Gear Oils

Contact Pressure = 0.9GPa, Temp. 80°C and speed 3 m/sec.
Steel ball on steel disc

Observed very low EHD traction values for the PAG product
Traction Measurement Experiments

Conditions
- Temperature = 80°C
- Slide Roll Ratio (SRR) = 0-50%
- Contact pressure = 1.25GPa
- Speed = 1 m/sec

Objectives
a) Compare EO/PO copolymers versus PO Homo-polymers
b) Assess if polymer branching from the initiator impacts traction behavior
c) Develop some PAG design rules for controlling traction

PAO base oil was used as a reference throughout the study
EO/PO PAG exhibits low traction values

Surprisingly the PO PAG exhibits much higher traction values
Fixed Diol Initiator & ISO-320 Base Oils

MTM Conditions: 1.25GPa, Temp. = 80°C, speed 1m/sec. Steel ball on steel disc.

- **PO**: exhibits much higher traction values
- **EOPO**: exhibits low traction values

PAO reference is a blend of PAO-6 and PA0-40 to create an ISO-320 grade

EO/PO PAG exhibits low traction values
PO PAG exhibits much higher traction values
Effect of Initiator – Fixed EO/PO ratio and ISO-150 PAGs

MTM Conditions: 1.25 GPa, Temp. = 80°C, speed 1 m/sec
Steel ball on steel disc

Branched (triol) structure exhibits higher traction values than “linear” (monol and diol) structures
Triol initiators – ISO150 PAGs

MTM Conditions: 1.25GPa, Temp. = 80°C, speed 1m/sec
Steel ball on steel disc

PO triol structures exhibit higher traction values than EO/PO Triol structures
MTM Conditions: 1.25GPa, Temp. = 80°C, speed 1m/sec
Steel ball on steel disc

Traction coefficient vs. SRR, %

- PO Triol
- PO Diols
- PO Monols
- Group III
- PAO2
- PAO1
- EO PO Triol
- EO PO Diol
- EO PO Monols
Hydrocarbon Oils

MTM Conditions: 1.25GPa, Temp. = 80°C, speed 1m/sec
Steel ball on steel disc

API Group III and IV Base oils

Narrow design space for hydrocarbon oils
PAG Chemistries from ISO-46 to 150

MTM Conditions: 1.25GPa, Temp. = 80°C, speed 1m/sec
Steel ball on steel disc

Wide PAG design space to control friction by varying the polymer architectures

PO Monol, Diols and Triols

EO/PO Monol, Diols and Triols
Design Rules

Generic Rules

Design Rules for EO/PO Copolymers
Measurement of Pressure Viscosity Coefficients

Apparatus
Falling needle high pressure viscometer
Measure viscosity at pressures to 50,000psi
Temperatures from 24 to 100°C.

Model for Calculations
Roeland Equation
Example of Effect of Pressure on Viscosity

Increasing pressure can lead to a significant increase in a lubricant's viscosity

Example for an ISO-68 PAG Base Oil

An understanding of high pressure rheology is important for gears, roller element bearings and cams
Low viscosity EO/PO PAG (Monol) shows low alpha values across the temperature range.
High viscosity EO/PO PAGs (Diols) again show low alpha values across the temperature range.
Alpha Values for OSPs (ISO-320 & 460)

Oil Soluble polyalkylene glycols (OSP) use butylene oxide as a building block.

High viscosity OSPs show higher alpha values across the temperature range.
Assessing the Correlation of Traction Coefficient & Alpha Values

Correlation between base oil traction value and alpha value at 80°C

But if designing energy efficient lubricants there is a potential practical dilemma. Do you select a fluid with low traction value or one with a high alpha value?
EHD Film Thickness Measurements

Assessed EHD Film Thickness for three formulated ISO-320 Gear Oils

a) EO/PO PAG
b) Synthetic hydrocarbon (H-C) (PAO)
c) OSP (Oil Soluble PAG)

Method to Measure Film Thickness

EHD Ultrathin Film Thickness Measuring Rig
- Steel ball on a sapphire disc
- Pure rolling conditions (SRR = 0%)
- Temperature 40, 80, 120 and 150°C
- Speed range is 0.005-3 m/sec
- Load 41N (max. Hertz Pressure is 1.25GPa)

Typical PAG base oil profile
Film thickness measured at 2m/sec
EHL Film Thickness Measurements for ISO-320 Gear Oils

Film thickness (nm) at 2 m/s and 40°C

- H-C: 1289 nm
- EOPO PAG: 1114 nm

Film thickness (nm) at 2 m/s and 80°C

- H-C: 455 nm
- EOPO PAG: 474 nm

Film thickness (nm) at 2 m/s and 120°C

- H-C: 209 nm
- EOPO PAG: 256 nm

Film thickness (nm) at 2 m/s and 150°C

- H-C: 135 nm
- EOPO PAG: 171 nm

EO/PO PAG forms thick films at higher temperature

Data generated courtesy of Powertrib
EHL Film Thickness Measurements for ISO-320 Gear Oils

OSP forms very thick films across the temperature range.
Conclusions

- Different polymer architectures can lead to broad differences in EHD traction values.
- Linear (Monol and Diol) EO/PO copolymers offer the lowest traction values.
- Branched (Triol) PAGs show higher traction values than linear structures.
- Lowest alpha values were observed for EO/PO copolymers.
- Correlation exists between alpha and traction values.
- OSPs seem to offer the ability to offer very thick films – more research ongoing.
- Tailoring designing PAGs offers the potential to create “building blocks” for formulators looking to develop energy efficient solutions of the future.
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