Fundamentals of Water Soluble Thickeners for Industrial Lubrication
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1. Introduction
1.1 Opportunities in Water-based Industrial Lubrication

Despite initial issues that come to mind with the idea of water as an industrial lubricant there a number of benefits in specialty applications where the unique properties of water can be leveraged.[1] This study is limited to solutions of water and non-ionic polymers. Emulsions, dispersions, and latex are employed in various industries to modify viscosity but this paper is limited to fundamental work.

Environmental Impact and EAL
The gradual accumulation of synthetic materials on land and in oceans has become an increasing concern to people, industry, and agencies. In lubrication, environmental acceptable lubricant (EAL) programs like European Ecolabel have created a system for guiding formulators to maximize both biodegradability and biorenewability.[2] Such programs support and legitimize the drive for more eco-friendly products.[3] **Figure 1** outlines the basic philosophy of EAL. EAL lubricants have relied primarily on based on hydrophobic bio-based and synthetic esters. A key challenge remains in the need to possess both the oxidative stability and high VI of waxy saturated fatty acid groups but also the low temperature behavior of unsaturates.[3] This must be done at low costs. The answer may lie in the hydrophilic portion of biomass.

Figure 1: Lifecycle of environmentally acceptable lubricants (EAL) from renewable beginning to biodegradable ending

Water-based products may be a middle ground for EAL that offers high oxidative stability with good low temperature performance when fully formulated with glycols.[4] Synovial fluid – water, hyaluronic acid, polysaccharide, and proteins – that protects bones from wear and absorbs shock is a naturally occurring tribological marvel that highlights the extreme potential of aqueous lubrication.[5] Man-made formulations are primarily water and water soluble thickener with an additive package. Many water soluble natural or synthetic polymer chemistries are susceptible to biodegradation by hydrolysis, oxidation, and microorganisms over time which prevents the accumulation of these polymers in the environment.[6] Degradation occurs by gradual breakage of polar ether, ester, and amide bonds which revert the polymer to oligomers and finally monomers.[6] C-C bonds can degrade if the molecule is small and soluble.[7]

Ecolabel does not cover water-based lubricants but the program is a relevant case study for anticipating the metrics required to claim "eco-friendly" or products with high biodegradability and renewability appropriate to their level of incidental contact to the environment. The 2014 and 2018 European Ecolabel for lubricants requirements are listed in **Table 1**, below, comparing each version's biodegradation/bio-renewable requirements.[8] [9] A consistent feature is that the increasing likelihood of product loss from incidental to total loss logically requires more stringent eco-friendliness.

The new 2018 guidelines simplify the original five categories down to three by expected loss of product.[9] These are areas where water-based lubricants may find use in environmentally sensitive use:

Total Loss Lubricants ("TLL") – chainsaw oils, wire rope, concrete release, total loss grease/lube;
Partial Loss Lubricants ("PLL") – open gear oil, stern tube, two stroke, corrosion coatings, partial loss grease;
Accidental Loss Lubricants ("ALL") – hydraulics, metalworking fluids, closed gear oil, and accidental loss grease.

In 2014, renewability was assessed by literally counting bio-based carbon atoms versus total carbon content. At least 45-70% bio-based carbon was required depending on the application. The 2018 provisions removed required wt% renewable content but the product must be >25% to claim "bio-based" or "bio-lubricant".[3] This change for 2018 increases the acceptability of biodegradable but not bio-based components. However, 'readily biodegradable' status is more demanding in 2018; 'readily biodegradable' now requires >60-70% biodegradation in 10 days rather than 28 days. Greases have reduced biodegradation requirements since they are less prone to be lost to the environment.

Table 1. Comparison of 2014/2018 Eco-Label requirements for biodegradability and % bio-based carbon in finished lubricants versus their likelihood of loss to environment.[8] [9]

Categorization by Lubricant Type		wt% Biodegradable*		wt% Renewable	
2014	2018	2014	2018	2014	2018
1 - Hydraulic Fluids, Tractor Oil	**Accidental Loss (ALL)**	>90% Readily <5% Unassessed	>90% Readily <5% Unassessed	>50%	Not required >25% to claim "bio-based"
2 - Grease, Stern tube Grease	+Closed gear, MWF	>75% Readily		>45%	
5 - Industrial/Marine Gear Oils	**Partial Loss (PLL)**	>90% Readily <5% Unassessed	>75% Readily <20%Unassessed	>50%	
4 - Two-Stroke Oil	+Corrosion coatings	>75% Readily <10% Unassessed		>50%	
3 - Chainsaw, Stern Tube Oil, Wire Rope, Concrete Release	**Total Loss (TLL)**	>90% Readily <5% Unassessed	>95% Readily <5% Unassessed	>70%	
	Any Grease		>80% Readily <15%Unassessed		

Terminology: * The balance wt% being inherently biodegradable.
  "Readily biodegradable" (aka "ultimately biodegradable"):
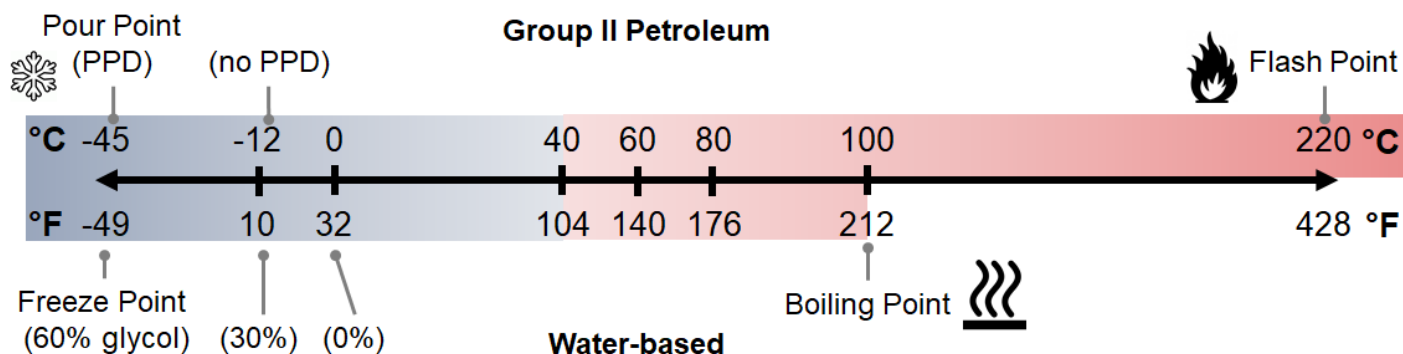 **in 2018**: 10 days, >70%, OECD 302; **in 2014**: 28 days, >60% loss by OECD 306/310 or >70% by OECD 301A
  "Inherently biodegradable": 28 days, 20-60% loss by OECD 306/310; >70% by OECD 302
  "Unassessed": Components considered "non-biodegradable, non-bioaccumulative" due to MW, particle size, solubility, etc.

Fire Safety

Figure 2 compares critical temperatures for both petroleum and water-based lubricants from -45°C to 220°C. At low temperature both systems can be improved by the use of cold flow improvers, either 0.1 – 2.0% of a polymethacrylate pour point depressant in the petroleum based lubricants or up to 60% glycol in water.

A water-based product could be formulated to the same freezing point as a petroleum product's pour point. This paper focused on pure water-polymer blends. Glycols and polyols are wide classes of components that modify freezing point but affect compatibility of the formulation.

Figure 2. Comparison of critical temperatures in petroleum versus water-based lubricants in °C/°F. Like paraffinic oil, water can operate at much lower temperatures with the aid of additives (PPD and glycol, respectively).

The highest possible operating temperature for a water-based lubricant at ambient condition is logically its boiling point, 100°C / 212°F. If water is kept under pressure then it will remain liquid to higher temperatures: 121°C at 29.4 psia (2 atm), 134°C at 44.1 psia (3 atm), etc.; this is the principle drives steam boilers and jacketed kettles.

Table 2 compares the high temperature hazards of various lubricant systems. Most liquid substances exhibit an appreciable vapor pressure, even below the boiling point, where a small fraction of the substance remains in gas phase above the liquid. Increasing temperature causes the amount of material at equilibrium in the vapor phase versus the liquid phase to increase. The flash point occurs when this ignition is confined to the vapor phase and is a momentary flash.[10] The fire point is defined as the temperature at which the flame is sustained over five seconds.[10] Higher still is the autoignition point at which the oxidation products released by the substance provide a spontaneous ignition source.

Table 2. Comparison of flash/flash/autoignition point of various lubricant chemistries
(via "Review of Ignition and Flammability Properties", Air Force Aero Propulsion Laboratory, 1968).[11]

Chemistry	Mineral Oil	Glycol	Water-Glycol	Polyalkylene Glycol	Phosphate Ester	Dibasic/Polyol Esters	Silicones
Flash Point	90 - 240°C 190 – 460°F	110 - 120°C 230 – 240°F	N/A	150 – 260°C 310 – 500°F	180 – 270°C 360 – 510°F	200 – 280°C 400 – 540°F	150 – 320°C 305 – 600°F
Fire Point	100 - 220°C 220 – 430°F	110 – 120°C 230 – 240°F	N/A	160 – 320°C 320 – 600°F	240 – 370°C 470 – 690°F	230 – 330°C 445 – 620°F	140 - 340°C 280 – 640°F
Autoignition	330 - 340°C 620 – 730°F	440 – 460°C 830 – 860°F	400 – 490°C 750 – 910°F	340 – 400°C 650 – 750°F	280 - 710°C 540 – 1300°F	370 – 430°C 705 – 800°F	300 – 510°C 570 – 940°F

This is not to say water has no high temperature hazards: a leak or rupture in pressurized high temperature water line will release superheated steam. Volatile additives in a water may also form vapor above the surface.

Temperature Regulation and Cooling
Heat originates from efficiency losses in pumping or frictional heating in confined hydraulic pumps and gear boxes. The process of converting energy into work is never 100% efficient. If a piece of equipment for transmitting mechanical power (say 100 kW / 134 HP) is 75% efficient then 25% of the equipment's power rating is lost as heat.[12] This loss effectively behaves like a 25 kW (34 HP) heating element.

The unique structure of water aids in temperature regulation. The extensive hydrogen bonding network of H_2O is much like a tough spring that must absorb high amounts of thermal energy undergo motion. Liquid hydrocarbons like petroleum oils have no polar or hydrogen bonding to dampen the effect of heating and rise in temperature with less energy. The specific heat capacity of water is defined as 4.186 J/g-°C (1.0 BTU/lb-°F) while a Group II oil is about 2.0 J/g-°C (0.48 BTU/lb-°F).[13][14] This means that water absorbs twice as much heat as petroleum oil per degree of temperature.

Evaporation of water can be a further safe-guard against overheat conditions. Boiling water is an endothermic and extracts an immense amount of heat (2260 kJ/kg or 974 BTU/lb) to cleave all hydrogen bonding between water molecules and impart enough kinetic energy for individual molecules to escape as vapor.

For example, consider a commercial 230 kg (507 lb) cast iron gear box with a 16.6L (4.4 gallon) sump of ISO 220 EP gear oil. It has a three-stage 14.2:1 gear ratio rated for 68 kW (91 HP) and is 96% efficient. In one hour, this unit generates 65.3 kWh (235,000 kJ) of work and 2.7 kWh (9800 kJ) of heat. Without cooling, this amount of heat would raise the oil and gear box temperature by 72°C. An equivalent volume of water, by the same math, would heat by 56°C. After three hours the oil gear box temperature would rise by 220°C and likely exceed the flashpoint. The water gear box would rise to 100°C by 1.4 hours of overheat but remain at 100°C as 6.8 kg of the 16.6 kg water sump evaporated.
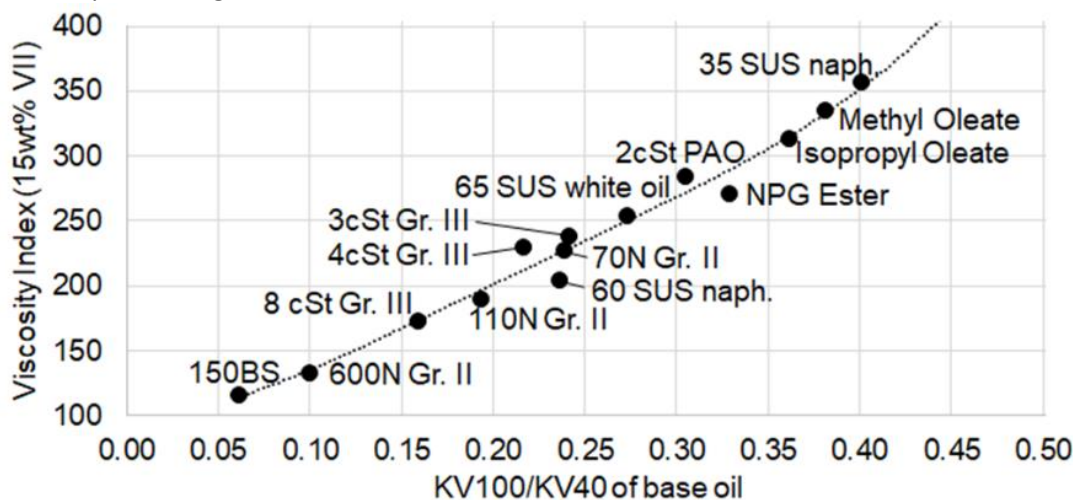
High Viscosity Index
Water is a very low viscosity fluid (KV40 = 0.686 cSt, KV80 = 0.412 cSt) and requires higher than average amounts of polymer thickener to build viscosity to a specific ISO VG. By comparison, petroleum oils are commonly available at starting viscosities of ISO 15 to ISO 460. Yet there are several advantages to formulating with certain low viscosity fluids.

A lower starting viscosity allows higher treat of VI improver without exceeding the desired ISO VG grade. Many VI improvers can offer a 200+ VI in Group II petroleum if high treat is applied but will result in a product that is far too

viscous. High VI, low viscosity products are difficult to formulate unless the starting fluid viscosity is suitably low and low viscosity petrochemicals pose flammability issues and GHS inhalation hazard labeling for KV40 < 20.5 cSt.

On a fundamental level, lower viscosity base fluids tend to yield higher viscosity indexes for a given wt% of VI improver. Functional Products has found that, more precisely, it is the KV100/KV40 ratio that determines the potential VI. **Figure 3** below reports the relationship between base fluid KV100/KV40 ratio versus VI for 15wt% polymethacrylate viscosity index improver (35% KRL shear stability). Base fluid KV40, KV100, or VI alone are poor predictors of potential VI with very poor correlation. Thus higher VI occurs most easily in products formulated with low viscosity fluids because low viscosity fluids tend to possess higher KV100/KV40 ratios.

Figure 3: Viscosity index after 15wt% treat of PMA VI improver versus starting KV100/KV40 ratio of the base fluid. The highest VI formulations are obtained from fluids with the highest KV100/KV40 ratio. Water KV100/KV40 = 0.6.

Water as a very low viscosity base fluid has very high 'potential VI'. Water is < 1 cSt but the KV100/KV40 ratio (approximating KV100 from KV40 and KV80 via ASTM D341) is exceedingly high at 0.60. This far greater than other low viscosity, high KV100/KV40 ratios that demonstrate high VI in formulated products: PAO2 (0.30), oleate esters (0.37), or low viscosity naphthenic oils (0.40).

These properties lead to water being an ideal low viscosity base fluid that can accept high amounts of polymer VI improver to maximize VI before exceeding the targeted viscosity grades which also exhibits very high potential VI according to its high KV100/KV40 ratio – all without posing the health and fire hazards of other low viscosity base fluids.

Logistics of Water
The availability and effective cost of water across the globe is a complex question with far-reaching social and economic answers.[15] The *2014 STLE Report on Emerging Issues and Trends* featured a questionnaire on Basic Human Needs.[16] Notably, this section was second-most popular at 640 responses, the first being the job outlook section (874). 'Water becoming of increasing value' was voted as a significant long-term concern (10+ yrs.) by 59%, 'reuse/recycling of water by 61%', and 'water filter availability' by 48%. The study found water as a vital resource will be a long-term trend.

Petroleum and synthetic base fluids, their performance, and pricing are often highly differentiated even per manufacturer due to different feedstocks, international trade, shipping costs, etc. Water, once isolated and treated, is simply H_2O with no variation in raw materials or isomers to fraction off. However, clean drinking water is the global priority; water for industrial lubrication should be sourced from non-potable or recycled 'gray water' whenever possible.

Since most water soluble components are highly polarized and have strong intermolecular attractions they are often powders in their dry form. These materials are ideal for shipping dry as formulated blends where the end user can reconstitute the blend on site. This strategy would negate the majority of shipping and fuel costs associated with transporting lubricants by only sending the performance additives and thickener as solids. Simply add water and stir.

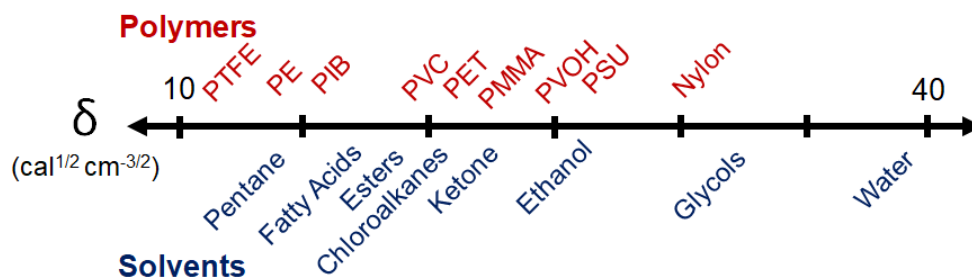## 1.2 Technical Challenges in Water-based Industrial Lubrication

The effect of water as a component or contaminant in industrial lubrication is complex. Water is often feared in many lube oil and grease applications.[17] [18] Yet water remains an integral part of many common lubricants and coolants: metalworking fluids, fire resistant hydraulic fluids, and glycol coolants. 'Raw-water' marine engines even cool with pure salt water. These systems utilize water as an economic medium to diminish fire hazard and provide excellent cooling.[1912] Key difficulties pertaining to the design of general purpose water-based lubricants using are detailed below.

Finding Water Soluble Chemistries

Multiple polymer chemistries can modify viscosity in a given base fluid so it is important to review many chemistries in broad surveys to find the best compromises in thickening efficiency, shear stability, VI improvement, and cost.[2021] This work covers water-based formulations from ISO 22 to ISO 680 to demonstrate the effect of polymer thickener / VI improver selection on treat rates and viscosity index. Petroleum-based lubricants use refined mineral oils as the base fluid and hydrocarbon polymers as thickeners. Water, as a new base fluid, requires unique additives and polymers specific to the high polarity and hydrogen bonding ability of H_2O. Time-tested polymer thickeners and performance additives for petrochemical-based lubricants will not dissolve into water and therefore entirely new chemistries must be sourced.

Hydrocarbon polymers, composed of carbon and hydrogen, dissolve into petroleum oils reliably with few exceptions due to the intuitive principle of "like dissolves like," a phrase dating back to at least the late 1800's.[22] Higher levels of quantitative theory provide a quantitative description of the interactions between solvent and solute. "Solute" is the component dissolved into the solvent. A close match between polymer and solvent ensures a more robust product capable of operating over wide temperature fluctuations and in combination with diverse additives without separation.[23] Several quantitative theories for understanding solubility were developed the mid-late 1900's.

Hildebrand's 'solubility parameter' method was a quantitative approach developed in the 1940's which assigns each solvent or solute a different solubility value along a sliding scale (**Figure 4**).[24] If the solubility parameter, δ, of solvent and solute are sufficiently close on this scale then a stable solution is expected.[24] Hildebrand solubility parameter is a useful first approach to finding solvents for different additives and polymers but has many exceptions. The solubility parameter is calculated from a material's cohesive energy density (the strength of the internal attraction of the material), whether it be high or low cohesion. Hildebrand theory assumes that if the cohesive energy densities of two materials A and B are similar then the molecules of A cannot tell the difference between molecules A or B and remain in a stable blend.[24] "Like dissolves like" and materials with high or low cohesion favor similar environments. A and B solubility parameters δ_A and δ_B are two dissimilar then the mixture of A and B will separate into a layers of A or B.

Figure 4. Polymers and solvents arranged by Hildebrand solubility parameter along a sliding scale. Compatibility is predicted when Δδ < 4. Note that few common polymers appear suitable for water according to Hildebrand.[24]
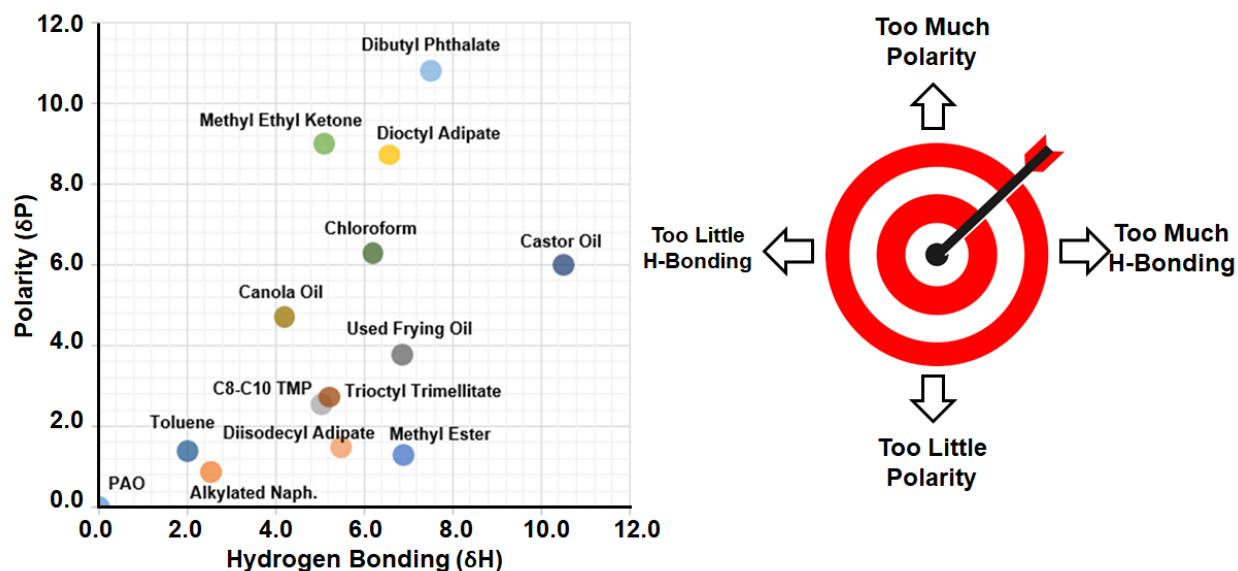
HLB theory, proposed by Griffin in the 1940's, is another single axis, sliding scale method for determining the compatibility of hydrophilic and hydrophobic materials in solution.[25] This method compares the percentages of hydrophilic (water soluble) and hydrophobic (water insoluble) features in the chemical structure. >10 is water soluble.[26]

Hansen, in the 1960's, divided Hildebrand's single parameter into three distinct contributions which describe different mechanisms for how molecules interact in blends.[27] δD, the dispersive solubility parameter, describes the interaction of hydrocarbons like linear or branched alkanes/aromatics and molecule size. δP, the polar solubility parameter, appears in polar molecules with high amounts of electron density such as those with C=O or halogens. δH, hydrogen bonding solubility parameter, results from a molecule's ability to accept or donate hydrogen bonds via protons in compounds like

amines, alcohols, amides, and acids. The square-sum of Hansen's parameters ($\delta D^2 + \delta P^2 + \delta H^2$) equals Hildebrand's parameter squared, δ^2. Splitting the parameter into three reveals a more nuanced picture of compatibility.

Figure 5 shows a two-dimensional plot of HSP δP and δP for many common fluids. Hansen solubility theory is applied in a similar manner as Hildebrand – the parameters, plotted like coordinates in space, must be suitable close between materials A and B.[27] The high level of detail in Hansen's approach explains unexpected results hidden in Hildebrand's single parameter approach. Knowing why solutions are incompatible allows a formulator to tailor a solvent by blending with co-solvents. Hansen solubility parameters are measured or approximated by systematically calculating D/P/H parameters based on each chemical group.[28]

Figure 5: A 2D plot of Hansen solubility can guide formulators in finding compatible blends in many industries (water: $\delta P = 16$, $\delta H = 42.3$). Polymers are stable when the solvent parameters are sufficiently close to the target: how close is close enough depends on the chemical structure and organization of the polymer.[27]

Thickeners and Shear

Water is a very low viscosity fluid (< 1 cSt at 20°C / 68°F) which must be thickened to a useful viscosity for a given application. Industrial specifications like ANSI AGMA 9005, DIN 51517, and ISO 12925 define the proper viscosity grade best suited to a given mechanical system's load, speed, and gearing.[29] Lubricants on high speed, low load equipment may be thinner than 15 cSt at 40°C (ISO 15) while heavy duty mining or drilling oils can exceed ISO 22,000.

High speed and high load applications will mechanically shear polymeric thickeners and reduce the viscosity of thickened lubricants over time. High molecular weight ("MW") polymers experience proportionally greater shear forces and therefore produce greater shear losses.[19] An improperly chosen thickener can lose substantial viscosity from lubricant's initial wear in and fall below specifications.

Polymer-modified lubricant is typically measured for shear stability. A specification may call for the product to remain in its ISO or SAE viscosity grade through the test and/or demonstrate a low % viscosity loss. Several test methods are available depending on the severity of the application.[19] Three commons methods are: ASTM 6278 Kurt-Orbahn diesel injector (for crankcase oils), ASTM D2603/D5621 sonic shear (for hydraulic fluids), and CEC L-45-A-99 tapered roller bearing ("20 hour KRL"; for gear oils).

Bio-Fouling

Water is the vital medium for most of life on Earth. Lubricants containing or encountering water are known to exhibit microbial growth. Additive packages containing carbon and heteroatoms (O, N, S, P, etc.) are suitable food for a host of bacteria, mold, and fungi that may enter the lubricant at any point from raw materials to end-user application.[30] The resulting effects are odor, physical slime or 'biofilm', and loss of performance.[31] A series of MWF-related sickness occurred in the 1990's and 2000's leading to increased consciousness for controlling microbe growth.[31]
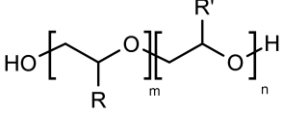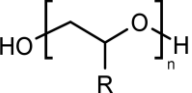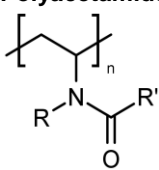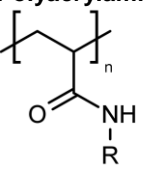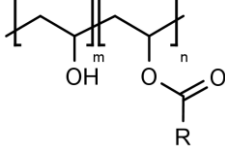
2. Experimental
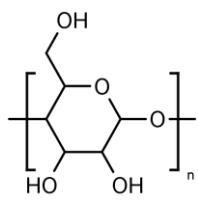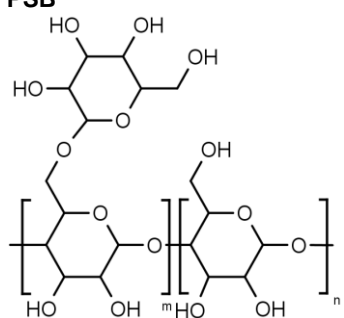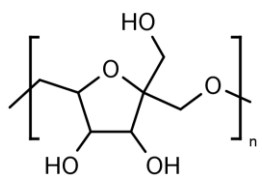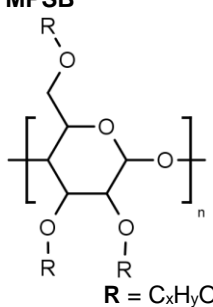### 2.1 Materials
Synthetic and Bio-based Polymers

Tables 3 and 4 below detail the naming and chemical structure of synthetic and bio-based water-soluble polymers. Eighteen polymers from seven chemistries were evaluated in water. Polymers were sourced as either dry powder or pre-dissolved solutions in water with known concentration. The exact MW and identity are proprietary.

Poor solubility was observed in the bio-based polysaccharides chemistries and necessitated processing with alkali or chemical modification to prepare water-polymer blends. Time, temperature, stoichiometries, and reagents to achieve rapid modification are proprietary.

Table 3: Chemistries and naming key for synthetic polymers evaluated in this study.

Poly alkylene glycol (PAG)	Polyether (PE)
"PAG1"–400 cSt, 50%WS/50%WI "PAG2"–1100 cSt, 60%WS/40%WI "PAG3"–17000 cSt, 75%WS/25%WI	"PE1" – Very Low MW "PE2" – Low MW "PE3" – Medium MW "PE4" – High MW
Polyacetamide (PAC)	**Polyacrylamide (PAM)**
"PAC1"–Low MW "PAC2"–Medium MW "PAC3"–High MW	"PAM1" – Very High MW
Poly alcohol-ester (PAE)	R = H or CxHy **"%WS"** = mol% water soluble monomer **"%WI"** = mol% water insoluble monomer

"PAE1"–Medium MW, 88%WS/12%WI
"PAE2"–Medium MW, 92%WS/8%WI
"PAE3"–Medium MW, 99%WS/1%WI
	MW (Molecular Weight): "Very Low"=< 1000;
	  "Low"=10k-100k; "Medium"=100k-200k;
	  "High"=300k-400k; "Very High" =1-10M

Table 4: Classes and naming key for natural and modified natural polymers evaluated in this study.

Natural Polysaccharides (PS)	Modified Polysaccharides (MPS)
"PSL" – Linear Polysaccharide "PSB" – Branched Polysaccharide	"MPSL" – Linear, modified by hydrolysis/isomerized "MPSB" – Branched via chemical grafting
PSL **PSB** 	**MPSL** **MPSB** R = CxHyOz

Water

Water for sample preparation was provided from filtered municipal tap water in Macedonia, Ohio. Filtration was accomplished at ambient temperature by a General Electric carbon block water filter kit (#GXWH35F; #FXHTC). The filter is rated to 25µm at 10 gallons per minute (37.9 LPM) with a 30,000 gallon (113,500L) service life.

2.2 Methods
Sample Preparation

Polymers were dissolved in filtered water in a tared glass beaker. Any evaporated mass of water was replaced with fresh filtered water. The majority of polymer chemistries were easily dissolved at 40-60°C / 104-140°F in one to two hours.

PAE polymer chemistry required heating at 80-90°C / 176-194°F for several hours. Each polymer was prepared as an ISO 680 – 1000 stock solution and filtered at 10 micron to prepare lower viscosity grades. No biocides were used.

Viscosity and Viscosity Index
Solution kinematic viscosities (KV) were measured by ASTM D445 Cannon-Fenske capillary viscometers in a temperature regulated oil bath (Koehler #K23376). KV at 40°C (KV40) and 80°C (KV80) were measured at multiple polymer concentrations. Viscosity index (VI) is normally calculated by ASTM D2270 from KV40 and KV100. KV100 could not be measured for water and was approximated using ASTM D341 from KV40 and KV80. ASTM D2270 and D341 are routinely applied to non-petroleum lubricants (ester, PAO, and PAG lubricants).

Clarity Measurement
Clarity was measured as turbidity in Formazin Nephelometric Units (FNU) by a Milwaukee Mi 415 portable turbidity meter. FNU turbidity quantifies the amount of infrared light scattered by haze in solution from a 90 degree angle.

Four-Ball Extreme Pressure and Wear
Extreme pressure of water-based lubricants with polymer and additives was measured using a 4-ball extreme pressure weld test ASTM D2783. Four-ball wear (D4172) at 20 kg load was used to characterize anti-wear behavior.
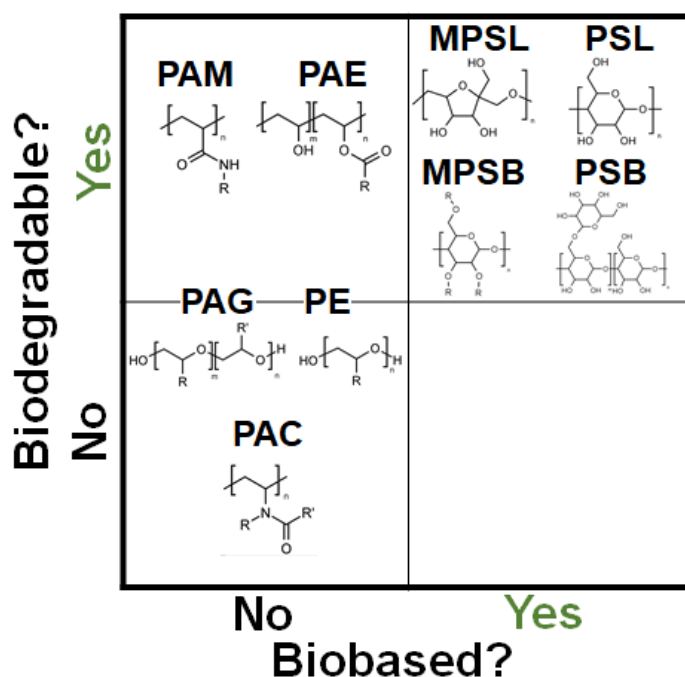
Simple Foam Shake Test
The effectiveness of defoamer chemistries was evaluated by adding 50g of ISO 46 water-polymer blend to a 100g jar. The jar was closed and shaken for 30 seconds. The sample was allowed to sit for one minute before checking for foam. Next, one drop (~0.005g) of defoamer was added and shaking was repeated. Difference in foam was noted subjectively.

3. Results and Discussion
Viscosity from Water Soluble Polymers
Figure 6 presents the nine chemistries arranged by their biodegradability and renewability ("eco-friendliness"). Not all biodegradable polymers are bio-based and vice versa. None were biobased without being biodegradable (i.e. polyethylene from ethanol-to-ethylene). EAL programs, like Ecolabel, may stress biodegradability over renewability. Biodegradability will vary by MW, end groups, and application. PAG and PE are biodegradable at low or very low MW.

Figure 6: Water soluble chemistries by their relative "eco-friendliness" (biodegradability and renewability).[6 32 33 34 35]

Table 5 compares the thickening rate of all synthetic/biobased polymer chemistries at ISO 46 and 460 with their VI. These viscosities are typical for hydraulic and industrial gear fluids. Normally thickening efficiency is compared between equal treat of 1wt% polymer in ISO32. Since MW varied from 10^2 to 10^7 this would produce a wide range of viscosities, some low and some high but most not useful.

Table 5: Comparison of synthetic and biobased water soluble polymer chemistries benchmarked by their required wt% treat to meet ISO 46/460 with VI.

Chemistry	Water Soluble Group	Polymer	MW	ISO 46 in H_2O		ISO 460 in H_2O	
				%polymer	VI*	%polymer	VI*
Synthetic Polymers							
PAG	Ether -O-	PAG1	Low	49-51%	N/A	N/A	N/A
		PAG2	Low	39-41%	N/A	73-77%	152
		PAG3	Low	26-27%	N/A	44-46%	334
PE	Ether -O-	PE1	Very Low	85-90%	127	N/A	N/A
		PE2	Low	42-50%	240	83-86%	200
		PE3	Medium	5.3-5.7%	252	10-10.5%	357
		PE4	High	2.8-2.9%	183	5.2-5.4%	309
PAM	Amide w/ Proton -NH(C=O)-	PAM1	Very High	0.95-1.05%	415	1.7-1.8%	359
PAC	Amide w/o Proton >N(C=O)-	PAC1	Low	27-29%	243	43-45%	218
		PAC2	Medium	12-14%	281	24-26%	308
		PAC3	High	6.2-6.6%	257	12.6-13.2%	292
PAE	Hydroxyl Ester -OH -O(C=O)-	PAE1	Medium	4.8-5.1%	251	7.2-8.9%	283
		PAE2	Medium	4.6-4.9%	230	7.9-8.2%	270
		PAE3	Medium	4.4-4.6%	222	7.4-7.8%	259
Biobased Polymers							
PS	Hydroxyl Ester Ring -OH -O(C=O)- C_xH_yO	PSL	Very High	0.40-1.0%	354	5.6-5.8%	415
		PSB	Very High	0.70-0.75%	194	1.2-1.3%	171
MPS	Hydroxyl Ester Ring -OH -O(C=O)- C_xH_yO	MPSL	Very Low	60-62%	60	71-72%	67
		MPSB	Very High	0.35-0.40%	72	0.64-0.66%	102

* Water-based VI calculated by ASTM D2270 using KV100 extrapolated from ASTM D341 with measured KV40 and KV80.

A few major trends exist in **Table 5**. Synthetic polymers tend to offer highest viscosity indexes (250 – 350) but treat rates generally range from >4% for ISO 46 and >8% for ISO 460. Biobased polysaccharides offer very high molecular weight which allows for very low treat rates (<1% for ISO 46, <6% for ISO 460) but VI is likely limited due to the low treat of polymer. A VI improver that thickens at a lower rate can be treated higher to ultimately produce higher Vis.
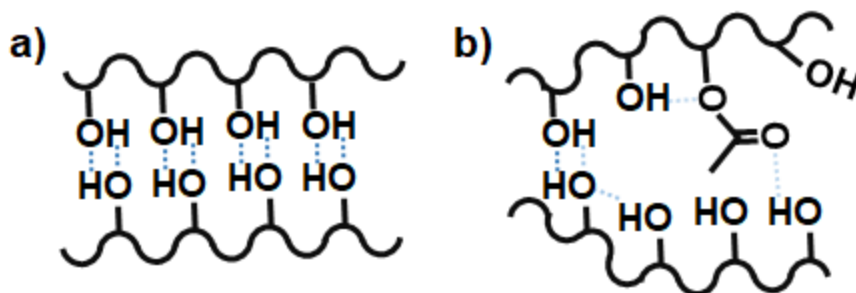
PAG polymers were tested at %WS/%WI ratios of 50/50 (PAG1), 60/40 (PAG2), and 75/25 (PAG3). These polymers were all found to be compatible in water at room temperature and up to 40°C. Above 40°C, each PAG demonstrated various extents of 'phase separation' where the blends separated into two layers – one polymer rich layer, one water rich layer. Kinematic viscosity at 80°C (KV80) could not be reliably obtained.

PE polyether blends were prepared using 100% WS monomer content. Unlike PAG chemistry, all PE polymers were found to be soluble at 40°C and 80°C which allowed measurement of viscosity index. The phase separation with PAG (50-75% WS monomer) into two distinct layers did not occur for PE chemistry (100% WS monomer). Instead, haze occurred below 40°C without separation. PE haze was corrected through a series of optimizations in **Appendix A**.

PAM chemistry was highly effective in both thickening water to ISO 46 and 460 with high VI despite low wt% polymer. The very high MW (1-10M) raises shear stability concerns which would make PAM most useful in a total loss or "single-pass" application. This complements the high biodegradability of the polymer. Unlike PAC, the other amide chemistry, PAM has amides with protons which form very strong intermolecular bonds – this is the basis of extremely tough polyamide fibers. This effect plus the very high MW made PAM very slow to dissolve but produce very good thickening efficiency. PAM would be difficult to deliver as a pre-dissolved concentration in water but emulsifying the PAM, like latex, may be a strategy for preparing very concentrated blends with relatively low handling viscosity for blenders.

PAC was the easiest solid synthetic chemistry to solubilize with 99% WS monomer PAE3 as the most difficult. Subjectively, the lab work in this study identified the ease of solubilizing trend as: PAG > MPSL >> PAC > MPSB > PE > PAE1 > PAM >> PAE2 > PAE3 >> PSB > PSL. PAG was in liquid form while PSB and PSL require alkali solubilization.

Figure 7 demonstrates why these polymers exhibit difficult during solubilization. **Figure 7** explains the phenomenon behind effects like poor solubility, haze, and foaming discussed throughout this work. Since PAC is a tertiary amide, >N(=O)-, it lacks a proton and cannot form strong hydrogen bonds between polymers such as PAE3 and PSL/PSB. PE polyether oxygen atom also lacks a proton but is difficult to dissolve due to strong hydrophobic attraction and orderly packing of the monomer units that must be unfolded by water and heat. PAC's bulky side group, much like PAE1, plasticizes the polymer by interfering with orderly packing of monomer units and facilitates easy mixing.
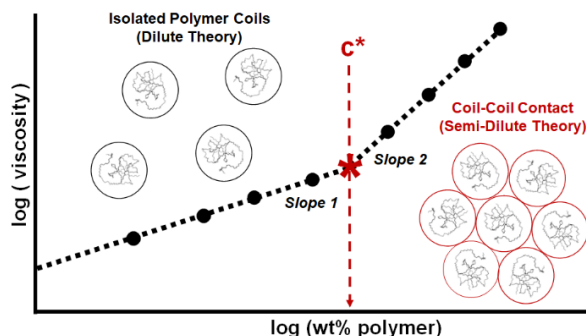

Figure 7: a) Polymers with polar/h-bonding monomers are difficult to dissolve due to the formation of extensive hydrogen bonding networks that must break down to dissolve (PAE3, PSL, PAM). b) The addition of bulky side groups (PAE1, MPSB, PAC) introduces high amounts of disorder to prevent the network from forming.

PAE chemistry was evaluated at varying alcohol/ester ratios from a single medium MW feedstock (PAE1 = 88% -OH, PAE2 = 8% -OH, PAE 3 = 1% -OH). Higher water soluble –OH content improves the thickening efficiency of the polymer despite lowering the total MW from loss of the bulky insoluble ester functionality. The polymer interacted with more H_2O through more –OH sites and became more soluble to provide higher viscosity. However, VI improvement decreases with increasing solubility of the polymer. This corroborates the common hypothesis for VI improvement as taught in literature and shown in previous work.[19][21] If viscosity index is driven by the contraction of polymer chains at low temperature and expansion at high temperature then further compressing the polymer would allow for even greater relative expansion. This is accomplished in various chemistries: including methyl methacrylate in polymethacrylates, styrene in styrene-olefin copolymers, or ester in the water soluble PAE. A slight amount of insoluble monomer causes the polymer chain to collapse further and thus allow for greater relative expansion at high temperature thus resulting in lower KV40 but higher VI.

PE and PAC show an interesting trend in **Table 5**. In both chemistries: low MW polymer yielded ISO 460 with lower VI than ISO 46 despite more polymer; medium MW and high MW ISO 460 VI was higher than ISO 46 VI; and peak VI for ISO 46 and ISO 460 were obtained with the medium MW grades. Previous work at Functional Products explained a complex qualitative relationship between the polymer concentrations and viscosity index in petrochemical lubricants.[21] The critical concentration, c*, at which polymer chains begin to touch in solution was attributed to peaks and maxima in the plot of wt% VI improver versus VI. c* represents a critical mass of polymer network surrounding base fluid.
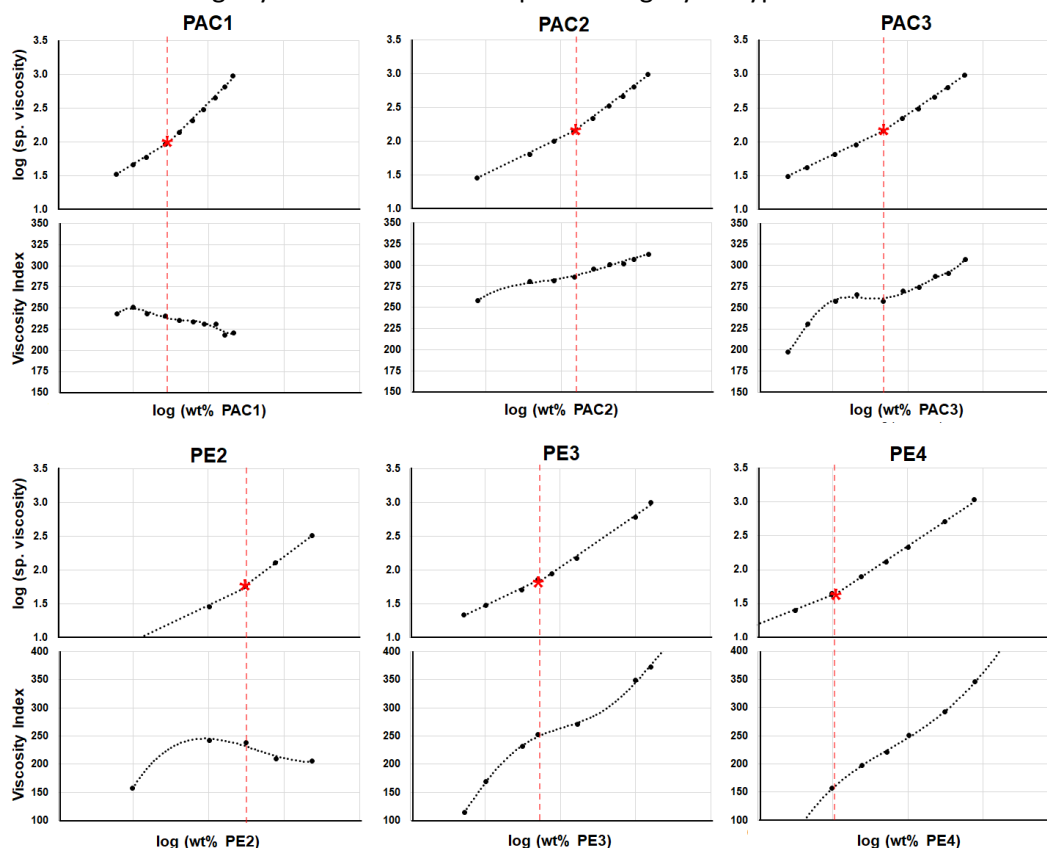
Figure 8 shows the structural origin of c*. Transitions like c* are identified by the first inflection point in log(viscosity) vs. log(wt%) plots.[36] 1/c* is the size of one chain, its intrinsic viscosity [η], also known as Staudinger index.[37][38] c* depends on MW by the Mark-Houwink equation: $[\eta] = 1/c^* = KM^{\alpha}$.[37][39] M is molecular weight while K and α are solvent quality parameters.[40]

Figure 8: c* is the transition point between dilute and semi-dilute solution theory. It occurs when increasing concentration of polymer coils move from isolation in base fluid to a continuous network around the fluid.

Figure 9 compares the c* inflection point on 'log (specific viscosity) vs. log (wt%)' with 'VI vs. wt% of PAC and PE.' The trend in ISO grade and VI for PE and PAC across varying MW grades can be explained from c*. The peak in VI occurs either briefly before or after c* and appears random regardless if the PAC and PE are low/medium/high MW. However, if one compares the length by number of repeat units, n, then the VI peak occurs after c* for short polymers and occurs before c* for long polymers.

Polymer length follows: PE2 < PAC 1 < PAC 2 < PAC 3 < PE3 < PE4. Short polymers PAC1 and PE2 (n = 50 – 400) continue to lose VI after c* with increasing wt% polymer. Medium-length polymers PAC2 and PAC3 (n = 1000 – 3500) exhibit a peak in VI before c* followed by a plateau in VI where c* occurs. Long polymers PE3 and PE4 (n = 4000 – 7000) do not exhibit a VI peak but c* occurs slightly before an inflection point along a $y=x^3$ type curve. VI does not reduce with

Figure 9: Critical concentration, c* (*red line*), is found at the inflection point of the log(specific viscosity) vs. log(wt% polymer) plot. Peak in VI vs. wt% polymer occurs close to c* and its behavior is highly dependent on the length by number of monomers, n, rather than MW, of the polymer. ISO 46 at log(sp. visc)=1.83; ISO 460 at log(sp. visc)=2.83.
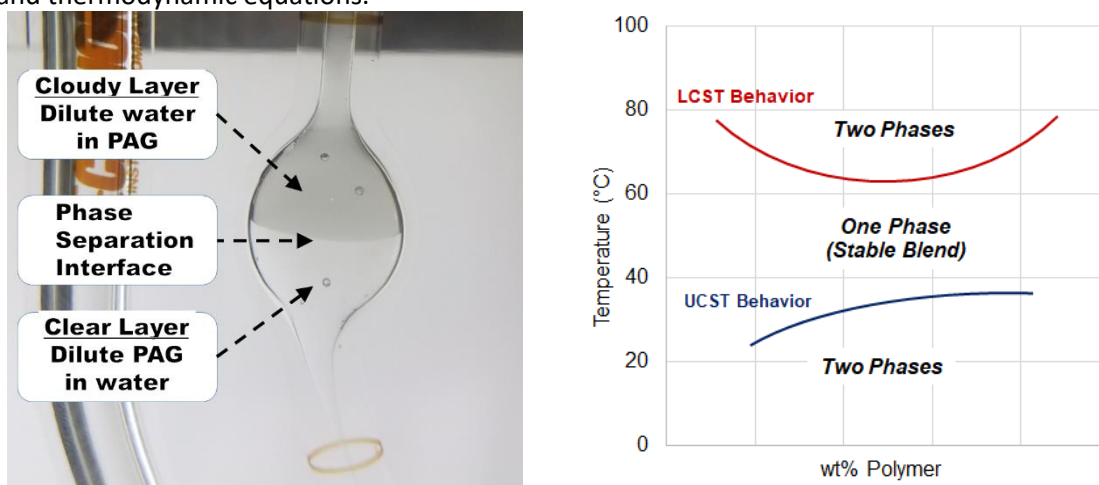
PS/MPS, natural and modified polysaccharide, required modification detailed in **Appendix B**. Overall, bio-based polysaccharides are cheap feedstocks with very low treat rates due to their very high MW (>1M) required to be a structural element of plants. Comparable MW grades in synthetic polymers are sold at a premium. Starchy polymers like PSL/PSB required processing with strong alkali to break the strong network of hydrogen bonded sugar units which hold the polymer network together like pulling apart hook and loop fastener. This process produced stable but hazy blends that did not settle over months of shelf time. Modified polysaccharides MPSL and MPSB were prepared from a PSL analogue for greatly enhanced solubility. MW reduction and isomerization in MPSL and grafting of water soluble groups onto MPSB provided clear and stable water-based solutions from ISO 22 – 680.

Cloud Point in PAG and PE Chemistries
Polyalkylene glycol copolymers (PAG) and polyether homopolymers (PE) exhibited a unique sensitivity to temperature which was not observed in other water-soluble polymers. Above or below a specific temperature for PAG and PE chemistry, respectively, the solutions transition from clear to cloudy. This transition is known as a cloud point and indicates complex temperature-dependent interactions between polymer and solvent.[41][42] Similar clouding can occur at ambient in petroleum oils with semi-crystalline olefin copolymers containing excessive ethylene, propylene, or styrene.

Polymer solutions which involve strong hydrogen bonding commonly exhibit cloud points – polyalkyene glycols/oxides are a classic example.[43] [44] If haze and separation occur when the temperature falls below a critical temperature then the behavior is described as an 'upper critical solution temperature (UCST)' and is reminiscent of the reversible low temperature gelation of components in oil at the pour point. If haze and separation occur above a critical temperature then the behavior is described as 'lower critical solution temperature (LCST)' and occurs most commonly in polar/hydrogen-bonded systems.

Figure 10 shows LCST-type phase separation in PAG4/water alongside a classic UCST/LCST phase diagram. LCST is uncommon – most polymers are more soluble with heat, not less – and indicates a unique balance of entropic disorder against order imposed by enthalpic attractions/repulsions. This effect has been described by both intuitive qualitative descriptions and thermodynamic equations.[41] [45]

Figure 10: <u>Left</u>: Phase separation of 20wt% PAG4 in water at 80°C during D445 capillary viscosity measurement. The separation results in a viscous cloudy layer (polymer/PAG rich phase) on top of a dense clear layer (water rich phase). <u>Right</u>: A classic phase diagram for UCST/LCST behavior.[41] The red and blue lines depict cloud point and vary in shape.

Water soluble PAG copolymers are convenient because the combination of two different monomers interrupts regular ordering of the polymer that manifests as crystallinity. This results in liquid, amorphous copolymers. The principle is similar to amorphous olefin copolymers which offer the best clarity and low temperature flow with a balanced mixture of roughly 50/50 ethylene-propylene. Pure polyethylene or polypropylene alone are highly crystalline and separate from petroleum oils to form gels. However, in the case of PAG one monomer is typically water insoluble (WI) and the copolymer becomes less soluble than the homopolymer.

Water soluble polyether/PAG is an exception, not the rule. Only certain PE/PAG polymers are uniquely soluble in water due to the ideal spacing of the ether oxygen along the polymer backbone.[44] This spacing coincides with the normal spacing of oxygen atoms in liquid water and allows the polymer to fit neatly into the water network despite high hydrophobic carbon content.

The two monomers commonly used in PAG copolymer synthesis are ethylene and propylene glycol. The trend for stability in water between EO/PO copolymers follows HLB rationale. Ethylene glycol has greater hydrophilicity due to the higher ratio of ether (-O-) and hydroxyl (-OH) which participate in hydrogen bonding with water versus the hydrophobic methylene units (-CH$_2$-) in the backbone. Propylene oxide has an additional –CH$_3$ group which reduces the solubility of the monomer. Propylene glycol itself is water soluble and stable but even low MW PPG/PPO exhibit rapidly worsening cloud points from 35°C with 1% PPG-1000 in water to 20°C with 1% PPG-2000.[46] Higher concentrations than 1wt% will lower the cloud point temperature by up to 10-15°C by 20wt% PPG.

PAG/water blends were clear and bright at room temperature but separated into two phases when heated. PAG1 separated into a thin clear phase and viscous hazy phase at 40°C (50/50 ratio of the two monomers) while PAG2 (60/40 ratio) was cloudy at 80°C. PAG3 (75/25) demonstrated concentration-dependent clarity at 80°C; concentrations at ≤ 20wt% PAG3 phase separated at 80°C but concentrations >40wt% were clear at 80°C.

Polyether (PE-) polymer chemistry is prepared from homopolymers of a water-soluble monomer which retains its water solubility even at high MW. However, the PE- series exhibits haze when the temperature is below the cloud point. High molecular weight polyether/water blends (PE-3 and PE-4) were hazy below 40°C but became clear when heated above 40-60°C. Low molecular weight PE-1 and PE-2 were clear at both room and elevated temperature. The lack of cloud point in PE-1 and PE-2 may be due to their preparation from the condensation of alkyl glycol which results in two very soluble –OH end groups; high MW PE-3 and PE-4 are prepared from the radical polymerization of alkylene oxide initiated by an alcohol which results in a less soluble alkyl end group.

Performance Additives

Table 6 details a water-based hydraulic fluid using a water/glycol base blend and VI improver. Base fluid and polymer alone do not make an industrial lubricant. Fulfilling the Stribeck curve's viscosity requirement for a given speed and load of application is just the start. The lubricant must fulfill several competing objectives through it's the suite of additives blended in: prevent corrosion of different metal, form ablative layers on the metal surface to prevent wear and scuffing with long-term use, release captured air to avoid foam, etc.

Table 6. Components of a basic water-based hydraulic fluid

Component	Primary Functions	Advantage(s)	Disadvantage(s)
Water	Fire resistance	Inexpensive, non-toxic	Very low viscosity; poor low temp. performance.
Glycol	Freezing point reduction	Economical	Poor film thickness; low viscosity Index
Polymeric Thickener	Viscosity Index improver; film thickness	Economical; Tailorable to various thickening efficiencies and shear stabilities	May exhibit inverse water solubility with temperature.
Additive Package	Corrosion Inhibitors (Fe/Cu); antiwear additives; dyes for leak detection; defoamer	Provides the necessary components for a fully functioning fluid	Package compatibility with water-glycol-thickener components

Anti-Wear / Extreme Pressure – Metal surfaces in close contact will produce wear with repeated operation over time. It is the goal of antiwear (AW) and extreme pressure (EP) additives to form sacrificial layers on the metal surface which are removed in place of metal.[19] Remaining additive in the bulk of the lubricant then migrates back to the freshly revealed metal to regenerate the protective layer.

Several ecofriendly components were evaluated at 0.5wt% for AW/EP and ferrous corrosion in **Table 7** with ISO 46 polyether (PE3 with optimal use of clarifier salt) in water. AW/EP additives for petrochemical lubricants are based on non-polar compounds: fatty acid esters, sulfurized fats and olefins, graphite, and oil-soluble metal complexes like ZDDP. Water-based lubricants require water-soluble components. These additives are typically water-soluble sodium salts of fatty acids, sulfur/phosphorus/oxides, or sulfurized triazines.[12]

Table 7: Performance of various biodegradable surface-active components (AW/EP/CI) in ISO 46 PE-water

Formula	4-Ball Wear Scar (D4172, 20kg)	4-Ball EP Weld (D2783)	Iron Chip Corrosion (D4627)
A: ISO 46 polyether PE3 in water	1.13 mm	315 kgf	10% rust
B: +0.5% Sodium Salt of Long+Short Chain Fatty Acid	1.24	250	~1%
C: +0.5% Sodium Salt of Long Chain Fatty Acid	0.76	250	3%
D: +0.5% Sodium/Sulfur Salt	1.10	250	~1%

The base formula (A) without further additives demonstrated a 315 kgf weld load by 4-ball EP (D2783) but showed high cast iron chip corrosion (D4627). The clarifier salt does act as an electrolyte which can either promote or hinder corrosion depending on their balance. Sodium fatty acid salts (B and C) improved chip corrosion significantly but reduced extreme pressure performance. The long chain fatty acid salts (C) were the best option for 4-ball wear scar. C18+ fatty acids form strong films on metal surfaces that allow the surfaces to slide without contact.

These formulas are not optimized but demonstrate that while each formulation might be the best of the four at either AW, EP, or CI, no one formula excels in two or more categories. Surface-active additives from these three areas must compete for the same real estate on the metal surface in order to perform their function. Surface area spent to absorb AW components is less surface area for corrosion inhibitors and so on. Formulators must balance and compromise.

Defoamers – Foam was observed in PAE and PE chemistry. Foaming in lab-scale experiments can complicate capillary-tube viscosity measurements. Foam in a lubricant can cause cavitation, poor heat removal, and reduction in the effectiveness of performance additives.[59] Foaming occurs from air which enters the product during circulation and mixing and remains held by the high surface tension in the lubricant. Foam shake tests are common among formulators looking to quickly assess foaming and optimize formulas before quantifying by laboratory methods like ASTM D892. A simple defoamer shake test was performed PAE and PE chemistries at ISO 46 solution with a silicone, butyl acrylate, and PAG defoamers. The PAG defoamer was the only chemistry effective at removing foam in the ISO 46 PAE and PE.

PAE alcohol-ester copolymers were found to cause the highest level of foaming among chemistries tested. The very strong foaming in PAE chemistry is likely due to strong hydrophilic like-like attractions between alcohol groups (-OH) along the polymer. PE polyether polymers had lower but noticeable foaming tendency. The ether (-O-) backbone of PE polymers can only accept hydrogen bonds so PE cannot form a strong hydrogen-bonded network like PAE. The foam formation was attributed to the same factors as cloud point: hydrophobic attraction between CH_2 and alkyl chain ends.

4. Conclusion

Water, as an eco-friendly base fluid, opens a wide spectrum of water soluble polymer chemistries with which to formulate. These polymers tend to be either highly renewable or biodegradable for environmentally acceptable lubricants (EAL) in applications like forestry, maritime, oil exploration, and other sensitive industries. Water itself is conducive to formulating very high viscosity index lubricants which may be supplied as dry solids for excellent economy on shipping.

The search for the best thickener system is a complex one in petrochemicals and more so in associative fluids like water which have unique hydrogen bonding and polarity. A number of promising chemistries from synthetic and natural origin demonstrate promise. Natural polymers tend to require extra processing but yield very high MW products with excellent thickening efficiency and biodegradability. More work is needed to develop convenient thickener/additive platforms. Water soluble additives for anti-wear, extreme pressure, corrosion inhibition, defoaming, etc. will follow similar solubility and selection rules as polymers. Sample formulations with additives demonstrated that surface-active components remain in competition with one another for metal surface contact in the water-based lubricant system.

Qualitative trends in wt% polymer and c* versus VI from previous work by Functional Products in 2018 was corroborated by more direct plots and analysis.[21] The relationship between c*, the critical concentration of polymer before coil overlap, was found to have a complex relationship with peak VI versus wt% polymer. Short polymers exhibit c* near the maximum VI with polymer followed by decreasing VI; medium polymers have c* in a temporary plateau in VI that slowly rises with additional treat of polymer; and long polymers show c* before an inflection point on a continuously rising plot of VI vs. wt% polymer.

Future work includes optimization of shear stable water-based lubricant formulations, development of opportunities for both the clear polyether viscosity modifiers and processed natural polysaccharides, and testing in relevant environments to explore further benefits/challenges to water-based industrial lubrication.
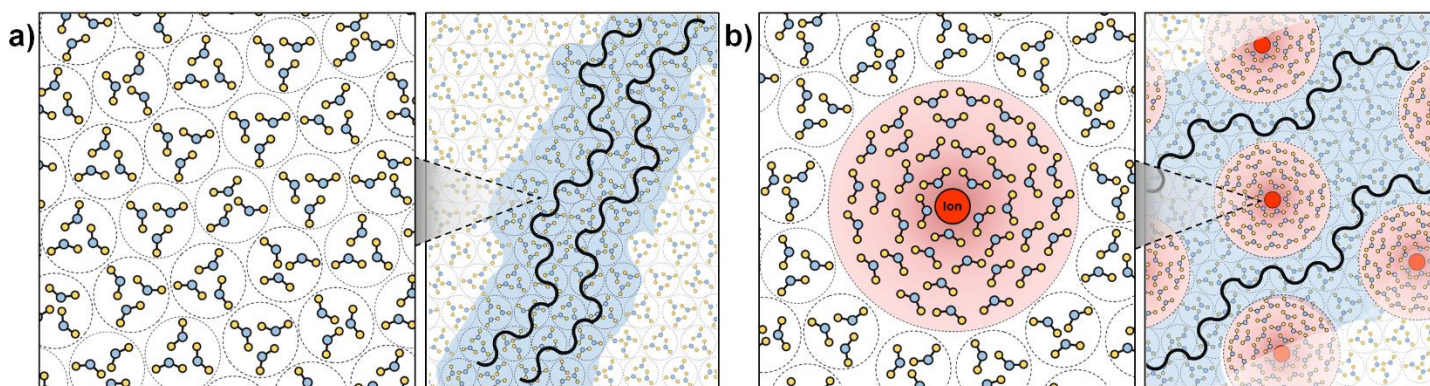
Appendix A: Modification of Polyether Cloud Point in Water

Cloud point is not an invariable behavior. The existence of a cloud point may be modified if the mechanism of haze formulation is understood and addressed.[47] Ten water molecules coordinate along every five monomers.[44] Two major features of polyether polymers dissolved in water are attributed to the formation of haze.

The first feature is the formation of a solvent 'cage' or 'shell' structure.[48] The solvent cage is a sheath of solvent around the polymer that carries the polymer in solution and screens the polymer from the bulk of the solvent and interaction with other polymers. Solvent cage strength varies – it may begin strong or weak and be altered by solvent conditions. Strong solvent cages have a high number of solvent molecules associated with each monomer to completely screen out other chain while weak solvent cages overlap and share multiple chains.[44] High or low temperature and resulting UCST/LCST behavior can weaken the solvent cage and allow hydrophobic attractions between chains to dominate which leads to polymer chain aggregate and cloud point.[48]
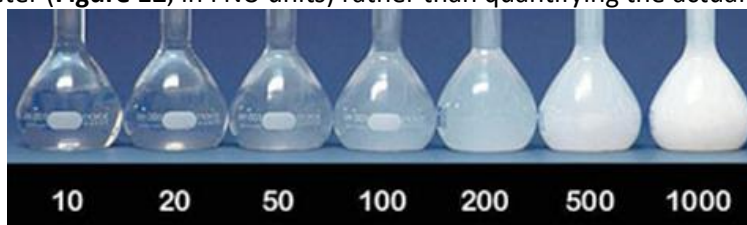
Solvent cage stability is influenced by the nature of dissolved species like salts, alcohols, and acids/bases which act as 'structure makers' or 'structure breakers'.[45][49] Ordinarily in water, H^+ and OH^- reorganize freely as a soup of atoms. Water molecules persist as weakly adsorbed clusters which percolate in and out of existence with a change in a single bond.[45] The structure of the solvent cage remains in flux between formation and dissociation. The addition of ionic salts imposes strong acid-base interactions between water and the dissolved ions. These interactions orient and polarize the individual water molecules granting the H_2O permanence as discrete, well-defined layers of structure surrounding the ionic core.[44][45]

Figure 11 compares the structure of normal and salt-modified water clusters (top) versus the resulting effect on solvent cage and polymer solution structure (bottom). In solutions, these salts improve the strength of the solvent cage by surrounding the polymer and cage with large stable water clusters rather than randomly percolating clusters. Select salts lower the cloud point by up to 40°C and tend to be large multiply charged anions, or small polar species like OH^- and F^-.[48]

Figure 11: a) Pure water (*blue-yellow*) exists as temporary clusters and make weak solvent cages (*blue*) around PE/PAG chains (*black lines*); b) Dissolved ions (*red*) impose structure via dipole interactions to form larger, more cohesive clusters.[45] 'Structure maker'-type ions strengthen the solvent cage and modify cloud point/haze.
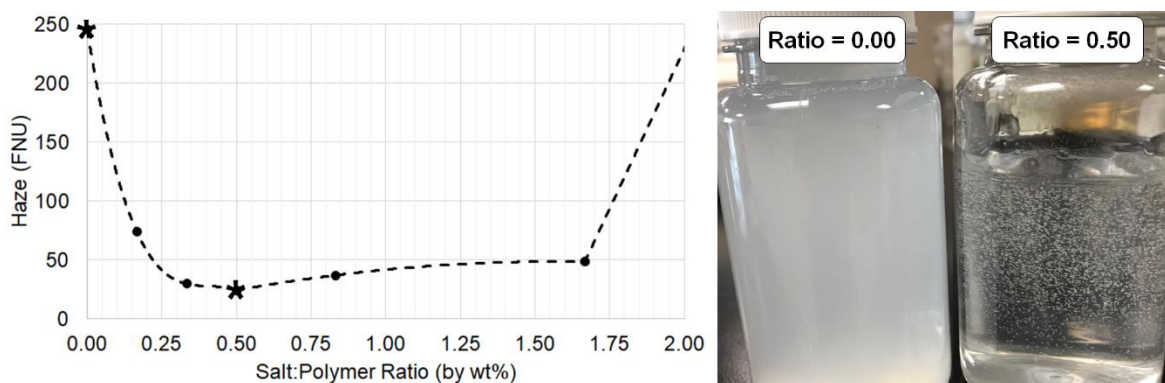
Cloud point modification with salt began with several wt% of medium MW polyether polymer (PE3) at ISO 15 treat in water as a control. Low viscosity was chosen to minimize polymer-polymer interactions and focus purely on polymer-solvent effects at relative dilute ISO grade. Progress in mitigating haze was evaluated by measuring clarity at room temperature by turbidity meter (**Figure 12**, in FNU units) rather than quantifying the actual cloud point.

Figure 12: Turbidity in FNU from 10 – 1000 units (modified from Optek.com). < 20 FNU is ideal for high clarity products while 30 - 50 units is detectable to the eye as slight haze. Haze is very often undesirable.

The ISO 15 formulation exhibited 246 FNU haze which appears as nearly opaque. Sodium and calcium acetate were added individually at 1 mole per liter (1M) treat from suggested starting concentrations in literature.[48] These salts produced no effect on haze likely due to their small size in solution. A high MW inorganic salt was tested next and appeared qualitatively effective at 1M. This salt appeared to meet the same structural elements of 'structure maker' salts in literature – large, complex anion related to mineral acids.[45][48] This salt will be referred to as "clarifier salt".

Clarifier salt concentration proceeded from the initial 1M treat to an optimization of varying wt% salt-to-polymer ratios in the ISO 15 preparation. **Figure 13** compares haze from the 'no salt' control (246 FNU) to an idealized ratio of 0.5 (1 part salt to 2 parts polymer) with 24.1 FNU. Haze improved rapidly from a ratio of 0 to 0.25 and remained low from approximately a ratio of 0.3 to 1.7 parts salt per part polymer in water. At 2.5 ratio the concentration of salt was sufficient to cause the non-ionic polymer to phase separate into a viscous cloudy layer (therefore an increase in haze). This occurred with gross excess of the clarifier salt at 5x to 10x optimal treat.

Figure 13: Haze in ISO 15 preparation of polyether polymer (PE3) with clarifier salt at varying mass ratios from 0 to 2.5. An optimal ratio is achieve at ratio = 0.5 (1 part clarifier to 2 parts polymer in water). The use of salt to reinforce solvent cage structure around the polyether polymer enables clear and concentrated PE water-based thickener with high VI.

The polyether polymer wt% was increased by a two-thirds to ISO 32 grade. This was designed to test if the ideal salt:polymer ratio and maximum salt content at phase separation were concentration dependent. Starting haze increased linearly with polymer wt% to 473 FNU at ISO 32. The optimal amount of clarifier salt was again a ratio of 0.25 to 0.5. Haze was minimized to 58 FNU which is 140% higher than the optimized haze in the more dilute ISO 15 preparation. This extra haze may be due to the hydrophobic clustering of chain end to polymer which becomes more favorable as more polymers dissolved.

Modification of the haze and cloud point in polyether-water blends was successful as demonstrated in the dramatic contrast between hazy and clear concentrations in **Figure 13**. Comparison of the dilute (ISO 15) and more concentrated (ISO 32) polyether with clarifier salt yielded a few major conclusions. The hypothesis that large complex anions will improve haze was affirmed. The ideal ratio was independent at ~0.50 for both ISO 15 and ISO 32 which implies the ideal total wt% of salt is dependent on polymer concentration. This fixed ratio would be convenient since concentrates of polymer and salt can be delivered together in proportion.
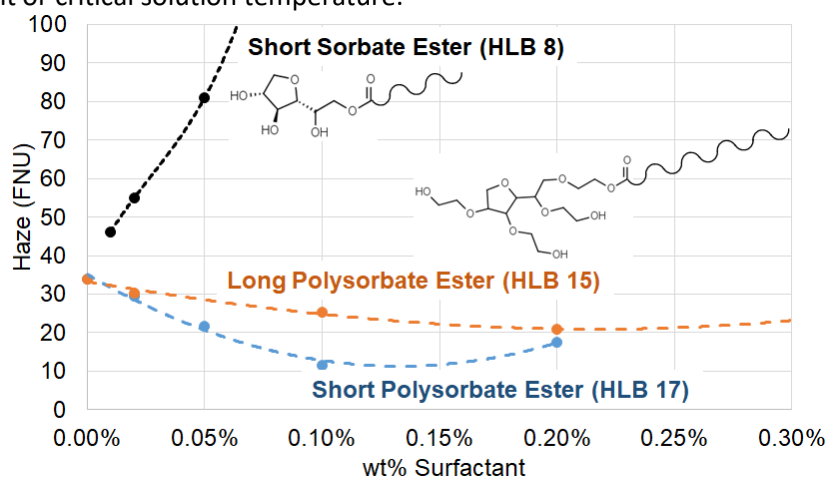
The salt strategy reduced, but did not eliminate, visible haze in ISO 15 and 32 by 90% from 246 to 24.1 FNU. Yet the formulations remained slightly hazy to the eye and ideally < 20 FNU would be considered "water-white" to an observer. The remaining 10% of haze must be attributable to a second haze mechanism.

The second feature of polyether-water solutions is hydrophobic clustering. Hydrophobic clustering of chain ends in polyether-water system occurs due to stray alkyl chain ends seeking out like-like attractions with the CH_2 backbone of other polyether polymers in water.[47] The alcohols used to initiate polymerization of the glycols can serve as a prominent hydrophobic site for clustering. These attractions lead to a network of clustered chains which can grow to a size that is detected by the eye.[47] The carbon-hydrogen groups along the polymer backbone are known to associate from one chain to another to minimize their unfavorable interaction with water. This effect can be reduced if a bifunctional diol initiator (i.e. ethylene glycol) is used instead. Terminating the chain in –OH's rather than $-OC_xH_y$ provides a hydrophilic chain end.

It was hypothesized that if this hydrophobic interaction could be provided instead by small molecule co-solvents or surfactants then polymer-to-polymer clustering would cease and this mechanism of haze formation deactivate. Using wt% glycol in excess of the polymer should produce conditions where the chain ends can more readily find a favorable glycol molecule rather than another chain to cluster with. However, 5-20wt% C3 or C6 glycol in ISO 15 PE solution was not effective. The C3 glycol is likely too hydrophilic to associate with the hydrophobic polymer chain ends. The C6 glycol is too hydrophobic and a 'structure breaker' by diluting the water.

Without success in glycol blending, it was concluded that the compatibilizer needs to have a larger hydrophobic segment to associate with the alkyl chain ends while also being highly soluble in water and not diluting out the ability of the water to hydrogen bond. The need for a single compound with two starkly different types of solubility lent itself to surfactant chemistry. The new hypothesis was that the chain end must be thought of as a species which needs to be emulsified into water with an appropriate surfactant, ideally as a clear micro-emulsion. It was decided to start testing with very small (<0.5wt%) concentrations since surfactants are concentration-dependent and the number of polymer chain ends to treat was a very small fraction of the total polymer content.

Sorbate and polysorbate fatty acid esters with long and short chain ("long" and "short") fatty acids were evaluated as bio-based emulsifiers to selectively disperse the polyether chain ends and prevent clustering haze. **Figure 14** demonstrates the effectiveness of three sorbate-based emulsifiers in reducing haze with polyether-water-salt blends. These species must 1) be water soluble; 2) not cause its own haze from wax-like interactions between fatty acid chains; and 3) have no cloud point or critical solution temperature.

Figure 14: Haze in ISO 15 polyether-water formulations with optimal (0.5 ratio) salt clarifier versus treat rate of three sorbate-based surfactants to aid in dispersing hydrophobic chain ends. The short chain fatty acid polysorbate was the most hydrophilic of the three and best suited to further reducing the haze to as low as 11.6 FNU at 0.10 – 0.15wt%. Short chain fatty acid sorbate without added ethylene oxide units was too waxy and too hydrophobic in water to dissolve without adding haze.

Long sorbate ester failed condition 1 as it was an insoluble waxy solid and could not be tested. Short sorbate ester failed condition 2 as it added considerable haze even at low < 0.10wt% treat. Lower HLB surfactant levels for more soluble surfactant required trying polysorbates. Both long and short polysorbates were effective in further reducing haze from the 24.1 FNU with optimal salt ratio. Long polysorbate ester gave a minimum of 20 FNU at 0.25wt% while short polysorbate ester gave 10 FNU at about 0.12wt%. These values (≤ 20 FNU) are virtually clear to the eye. Clarity reduction reverted with increasing treat beyond these values.

Starting from an initial 246 FNU, the combination of 'structure maker' salt and polysorbate surfactant to emulsify the chain ends reduced haze to 11.6 FNU (-96%) and fulfilled the goal of water-white (< 20 FNU) polyether blends. Approximately 90% of haze was attributed to solvent cage effects and 6% to chain end clustering. Further work is required to determine how the surfactant treat varies with polymer concentration and affects foaming.
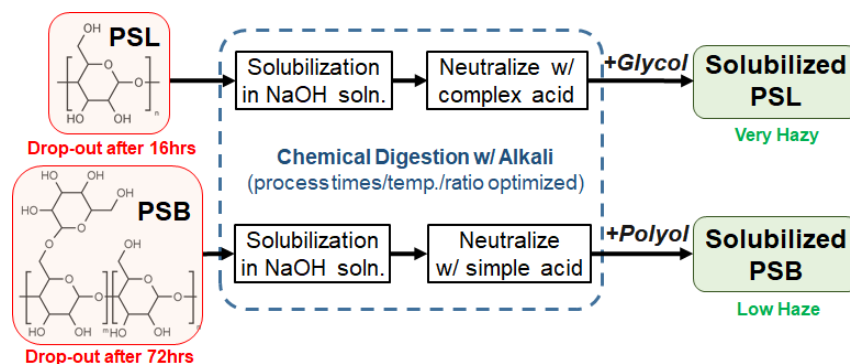
Appendix B: Modifying Polysaccharides for Improved Solubility

Polysaccharides, or starches, are polymeric carbohydrates produced from the coupling of sugars in plants and other organisms. These materials are commonly used to thicken and texturize foods or coatings.[50] High biodegradability and renewability from natural feedstocks makes this class of polymers highly attractive for eco-friendly applications. Like any bio-based product, the exact composition depends on the feedstock. In most cases the sugars are a 5-member ring with one ether (-O-) and four hydroxyls (-OH) or a 6-member ring with an additional hydroxyl. The polymers can be linear with sugar units in a row (like polyethylene) or branched with some sugars attached as side groups (like polybutene).

However, polysaccharides are difficult to process for industrial applications.[51] While the polymers contain very high levels of water soluble hydroxyl groups these polymers also contain large amounts of hydrophobic carbon backbone. High like-like attraction and repulsion from water results in tightly attracted polysaccharide chains which resist the work of solvents and make starches far less soluble than expected. This study includes a comparison of natural linear vs. branched polysaccharides, their solubility, and how to better process these materials for water-based lubricants using chemical modification.

Processing the natural polymers began with simple solubilization of the polysaccharide PSL at various temperatures from 20°C to 100°C. This resulted in opaque dispersions of particulate which prevented viscosity measurement. The dispersions separated during settling overnight at room temperature. Glycol, polyglycols, and fatty acid sorbitan esters were added at up to 70wt% in water – as guided by Hansen solubility calculation – to improve the solubility match between solvent and polymer. No improvement in clarity or stability was observed.

Strong bases are useful in disrupting the undesirable like-like attraction between linear polysaccharide chains and improving water-polymer compatibility.[52] [53] **Figure 15** outlines the alkali/glycol solubilization developed to improve PSL/PSB stability. Chemical digestion with base can improve solubility by providing hydroxide ions (OH$^-$) which are small, strongly interacting hydrogen bond partners that out-compete polymer-polymer interactions and allow tightly bonded chains to separate. Partial base-catalyzed hydrolysis of the backbone also reduces polymer size and improves processability by decreasing the number of hydroxyls per polymer chain as they become shorter.

Figure 15: Workflow for solubilizing of PSL and PSB to more soluble and stable water-based thickeners with high bio-based content and thickening efficiencies. Haze remains but is treated by adding an appropriate co-solvent.

The linear polysaccharide PSL was digested by mixing with heat and a low concentration of strong base at pH 13 for a period of time. The highly alkaline solution was clear with a slight orange tint. Neutralization was performed with acid. Addition of organic acid to reach pH 7 resulted in a viscous, hazy liquid upon further stirring. Milky-white ISO 220 with VI 417 and ISO 46 with VI 354 were prepared at 5wt% and 0.5wt% dissolved solids. These samples remained stable for several months. The addition of a glycol co-solvent and neutralizing with a complex inorganic acid similar to the PE clarifier salt improved clarity qualitatively though haze remained above 1000 FNU.
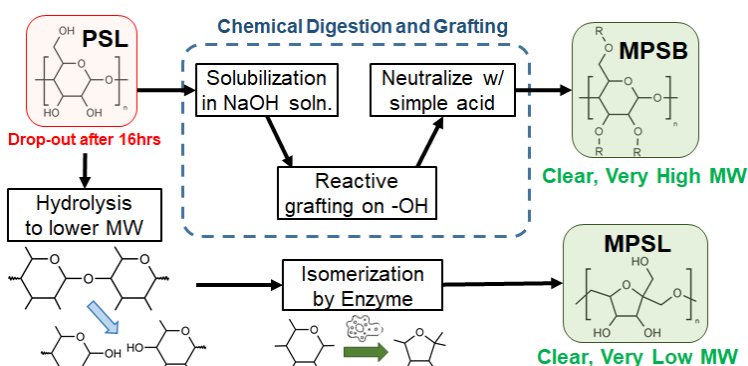
Branched polysaccharide PSB was investigated following the optimization of linear polysaccharide processing. Initial testing of simple water-PSB blends demonstrated better clarity and posed greater promise as a clear bio-based thickener after optimization. PSB treat rate for ISO 46 and ISO 460 were found to be 25% and 80% lower than PSL for ISO 46 and ISO 460, respectively. Separation of initial PSB-water blends occurred after three days of standing – an improvement over 16hr separation in PSL. Chemical digestion by alkali further improved storage stability to months but remained

hazy. Testing various glycol/polyol co-solvents and acids revealed that PSB is better optimized than PSL. Very low but appreciable haze (30 – 100 FNU) was observed with alkali-treated PSB at ISO 46 in water. However, VI was observed at roughly 200 points lower than PSL as same viscosity: typically VI 150 to 200 with a peak of 250 at ISO 100.

Chemical digestion with alkali/acid and various glycol co-solvents on PSL and PSB was effective in increasing stability. However, the initial issues with drop-out and remaining haze after optimization necessitated more aggressive chemical modification of the polysaccharides to ensure higher solubility, stability, and clarity. It is worth noting that moderate solubility and drop out of the polymer can actually be beneficial in bio-based proppants for hydraulic fracking where the particulate aids in wedging open cracks in shale gas deposits.[54] [55]

Figure 16 outlines the chemical modification of natural polysaccharides to produce MPSL and MPSB polymers.[51] The chemically modification resulted in derivatives with excellent solubility and clarity in water. The process and results for two modified derivatives a described below. Many processes exist to modify polysaccharides in the effect to enhance their solubility and usefulness as alternatives to petrochemicals. Most processes entail reaction of the hydroxyl (-OH) groups, or hydrolysis of the ether (-O-) linkages to depolymerize the polysaccharides into lower molecular weight and more soluble byproducts.[56] [57]

Figure 16: Workflow for chemical modification of polysaccharides to obtain thickeners with high efficiency and exceptional clarity in water. Graft in alkali solution retains the very high MW while isomerization reduces MW.

Low molecular weight ISO 680 polysaccharide thickener MPSL was prepared by cleaving the polymer backbone and isomerization of the six-ring sugar monomers to more soluble five-ring sugar with catalyst. The choice of sugars in the polysaccharide may be a key factor in water solubility of the polymer: of the monosaccharides, fructose is 1600% more soluble than lactose and 300% more soluble than dextrose/glucose.[57] The process is reminiscent of the catalytic breakdown and reassembly of Group III synthetic petroleum oils. Due to the low molecular weight this sample required high treat rates (59wt% = ISO 32) in water. No significant VI improvement was observed with VI 50 – 80 over the ISO 22 – 680 range. This material should be prepared at higher MW in the future but may serve as a shear stable thickener when combined with synthetic VI improvers described previously.

Grafting of water soluble side groups onto polysaccharide was used to prepare MSPB. Changing the chemistry rather than MW produced far greater thickening efficiencies than MPSL. This process was achieved by continuing the chemical digestion in base described previously and treating the dissolved polysaccharide with a water soluble reactive monomer that branched from the hydroxyl side groups. Solubility improvement was attributed to three factors: 1) increasing the fraction of water soluble composition (HLB); 2) consuming the strongly bonding hydroxyl groups along the polysaccharide chain to weaken the strong like-like attraction between chains; and 3) the grafting of longer side groups to the backbone also acts to plasticize or 'soften' the polymer. Point 3 is seen with free flowing but high MW liquid polymers like polymethacrylates and polyalphaolefins.[58] Polysaccharide grafted with water soluble side groups maintained the high thickening / low treat performance of the branched natural polysaccharide but produced clear solutions. VI from ISO 22 – 680 fell within a narrow range of 200 – 220.

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