Fundamentals of Water Soluble Thickeners for Industrial Lubrication

Erik Willett, PhD; Daniel Vargo; David DeVore
Functional Products Inc.

FUNCTIONAL PRODUCTS INC.
Innovative Chemistry for Lubricants
functionalproducts.com
1-330-963-3060
Macedonia OH, USA

1. Introduction

Water's role as a either component or contaminant in industrial lubrication is complex. Water is often feared in many lube oil and grease applications.[1] [2] Yet water remains an integral part of many common lubricants and coolants: metalworking fluids, fire resistant hydraulic fluids, and glycol coolants.[3] [4] These aqueous systems utilize water as a cost-effective medium for diminished fire hazard, excellent cooling, and high lubricity when properly formulated and applied. Water offers many unique opportunities and challenges to industrial lubrication.[5]

Environmentally Acceptable Lubricants

The accumulation of synthetic materials on land and at sea has become an increasing concern. Environmentally acceptable lubricant (EAL) programs like European Ecolabel outline specifications for biodegradability and renewability in lubricants to be used in sensitive applications like maritime and forestry .[6] [7] **Figure 1** depicts the basic philosophy of EAL. These products have primarily relied on plant or animal triglycerides and synthetic esters of such fatty acids.

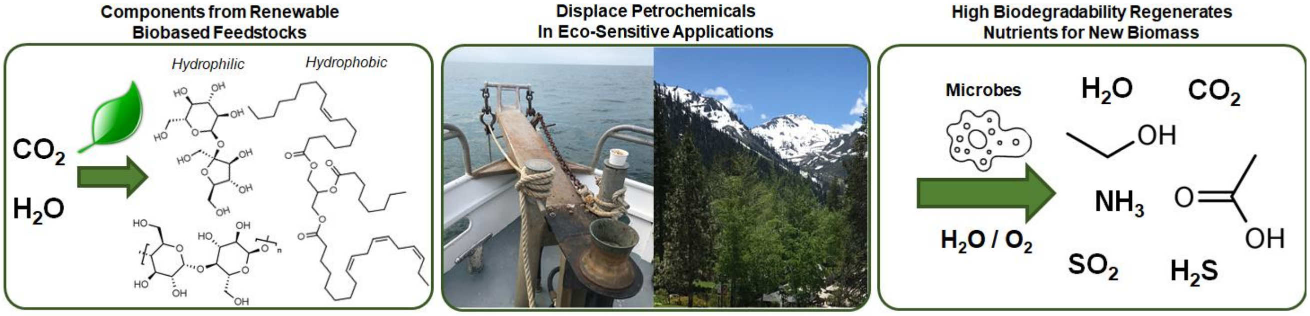


Figure 1: Lifecycle of environmentally acceptable lubricants (EAL) from renewable beginning to biodegradable ending

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.[7] The answer may lie in the hydrophilic portion of biomass – sugars, starches, and gums – rather than fats. Water-based products offer high oxidative stability with good low temperature performance when formulated with glycols.[8]

Many water soluble biobased 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.[9] Degradation occurs by gradual breakage of polar bonds which revert the polymer to oligomers and finally monomers.[9] C-C bonds can degrade if the molecule is small and soluble.[10]

The question persists on how to account for the 'biodegradability' of water in a formulation. Ecolabel does not currently extend to water-based lubricants but the program remains a relevant case study for anticipating the required 'eco-friendliness' of lubricants according to their application and likelihood of loss to the environment.[11] [12]

Fire Safety

Figure 2 compares critical temperatures for both petroleum and water-based lubricants from -45°C to 220°C.

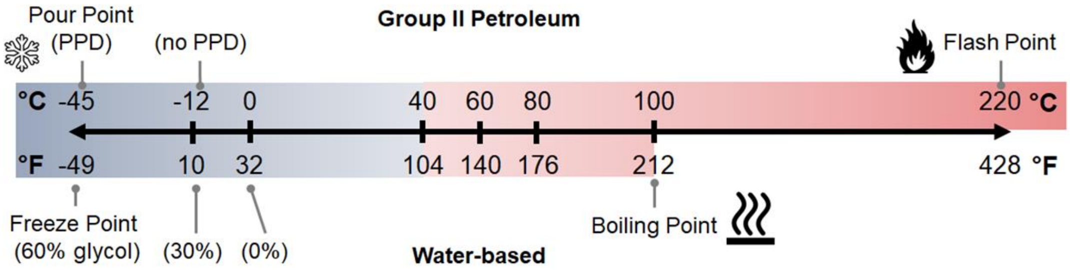


Figure 2. Features in the temperature-behavior relationship of petroleum oil versus water-based lubricants.

At low temperature, the pour point of both petroleum and aqueous systems are limited but can be improved by the use of cold flow improvers: 0.1–2% of pour point depressant in mineral oil or up to 60% glycol in water.

The highest possible operating temperature for a water-based lubricant at ambient condition is logically its boiling point, 100°C / 212°F. Pressurized water can remain liquid to higher temperatures as is the principle behind steam boilers and jacketed kettles. Petroleum products have higher operating temperatures which are ultimately limited by the flash point. This does not mean 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.

Table 1 compares the high temperature hazards of various lubricant systems. Most liquid substances exhibit a flash point when trace vapors above the liquid are in sufficient concentration to allow a momentary flash in the presence of an ignition source.[13] Higher temperatures create more vapors and leads to the 'fire point' when the surface burns for over five seconds.[13] The 'autoignition point' occurs when the heat of the oxidation products alone can ignite the vapor.

Table 1. Comparison of flash/flash/autoignition point of various lubricant chemistries.[14]

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

Reproduced from: "Review of Ignition and Flammability Properties", Air Force Aero Propulsion Laboratory, 1968

Temperature Regulation

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 100 kW / 134 HP pump is 90% efficient then 10% of the power rating is lost in the form of heat as if it were a 10 kW heater.[4]

The unique structure of water aids in temperature regulation to mitigate this heating. The extensive hydrogen bonding network of H_2O allows water to absorb high amounts of heat without changing much in temperature. 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).[15 16] This means it takes twice as much heat per degree to heat a mass of water toward overheating versus petroleum. Evaporation of water can be a further safe-guard against overheat conditions. Boiling water is endothermic/cooling process and extracts large amounts of heat (2260 kJ/kg or 974 BTU/lb). This thermal energy is used to separate hydrogen bonded water molecules and impart enough kinetic energy for those molecules to escape as vapor.

Bio-Fouling

Lubricants containing or encountering water are known to exhibit microbial growth since water is the medium for growing life on Earth. Additive packages containing carbon and heteroatoms (O, N, S, P, etc.) are suitable food for a host of bacteria, mold, and fungi.[17] The results are odor, physical slime or 'biofilm', and loss of performance.[18] A series of MWF-related sickness occurred in the 1990's and 2000's leading to increased awareness of microbial spoilage.[18] Microbial activity is typically halted by the use of biocidal additives during the lubricant's use and storage.

Logistics of Water

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.

However, the availability and effective cost of water across the globe is a complex question with far-reaching social and economic answers.[19] The *2014 STLE Report on Emerging Issues and Trends* featured a questionnaire on Basic Human Needs.[20] 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.

Availability of Water Soluble Chemistries

When developing for new base fluids the best approach is often to survey a wide number of compatible polymers to find the best compromises in performance and cost before continuing to build out formulations.[21] [22] Viscosity modifiers in petroleum oil are typically hydrocarbon polymers due to “like dissolves like,” a phrase dating to the 1800’s.[23] Esters favor unsaturated polymers with C=O and C=C. Following this principle, H_2O structure suggests polymers should have hydroxyl (-OH) and ether (-O-) groups. Yet many polymers compatible in both water, petroleum oil, and ester are exceptions. Several numerical approaches to solubility were developed in the 1900’s to better guide selection.[24]

Hildebrand’s ‘solubility parameter’ method from the 1940’s assigns each component a different solubility value along a sliding scale (**Figure 3**).[25] If the solubility parameter, δ, of solvent and polymer are sufficiently close on this scale then a stable solution is expected. Comparing a single number for solubility continued to provide notable exceptions.

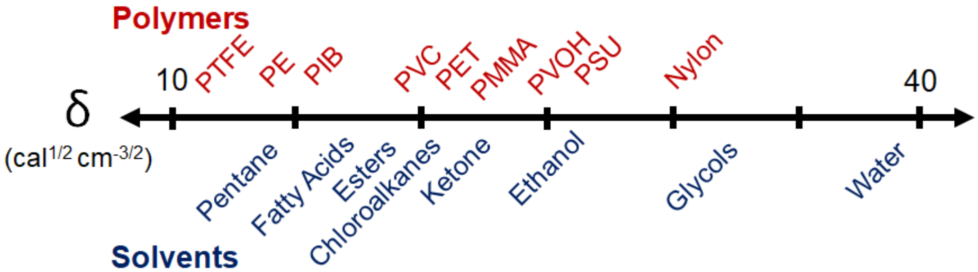


Figure 3. Polymers and solvents arranged by Hildebrand solubility parameter along a sliding scale. Compatibility is predicted when $\Delta\delta < 4$. Note that few common polymers appear suitable for water according to Hildebrand.[25]

HLB theory, proposed by Griffin in the 1940’s, is another single axis, sliding scale method that compares the percentages of hydrophilic (water soluble) and hydrophobic (water insoluble) features in the chemical structure.[26] >10 is water soluble.[27] This method is fairly intuitive, simple to apply, and a cornerstone of emulsion sciences.

Hansen, in the 1960’s, divided Hildebrand’s parameter into three different δ solubility parameters.[28] δD, dispersion, describes the effect of branching and size in hydrocarbons. δP, polarity, arises from electron-rich molecules containing oxygen like esters (>C=O), halogens (F/Cl/Br), or aromatics. δH, hydrogen bonding, occurs where molecules bind together at hydrogens on amines (>NH), alcohols (-OH), acids (-COOH), and amides (-NH(C=O)-).[29] Hansen theory contains a high level of detail but explains inconsistencies in Hildebrand and HLB theory.

Figure 4 shows a ‘map’ of Hansen’s δP versus δH for many fluids. For reference, water is $\delta P=16$ and $\delta H= 42.3$. The δP and δH coordinates of additives must fall within target of base fluid solubility to be compatible.[28]

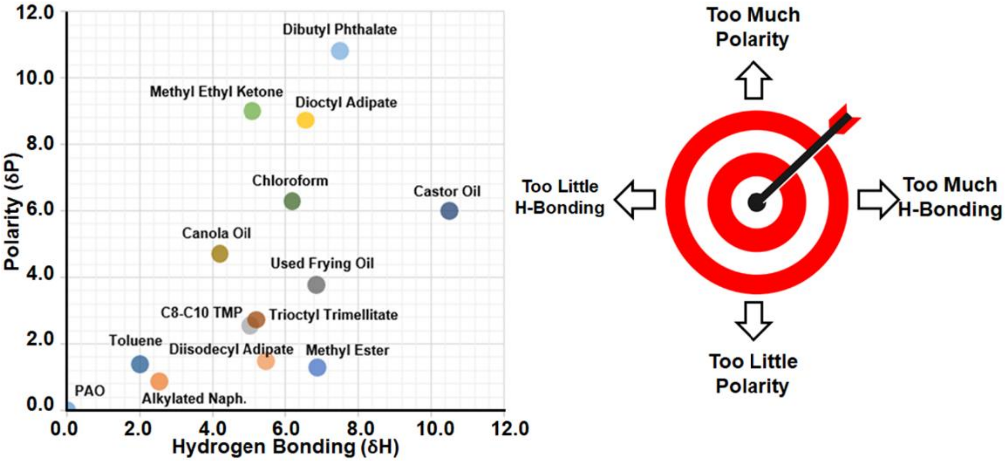


Figure 4: A 2D plot of Hansen solubility. Polymeric thickeners are stable when the solvent parameters are sufficiently close to the target: how close is close enough depends on the chemical structure and organization of the polymer.[28]

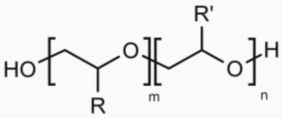
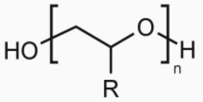
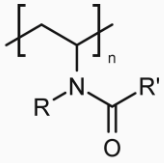
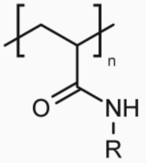
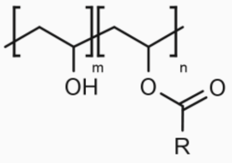
2. Experimental

2.1 Materials

Synthetic and Bio-based Polymers

Tables 2 and 3 detail synthetic and biobased water-soluble polymers identified by the solubility methods previously discussed. Eighteen polymers from seven chemistries were evaluated. Polymers were sourced as either dry powder or pre-dissolved solutions of known wt% in water. The exact MW and chemical identity are proprietary.

Table 2: Chemistries and naming key for various grades of synthetic polymers evaluated in this study.

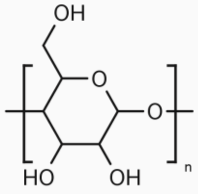
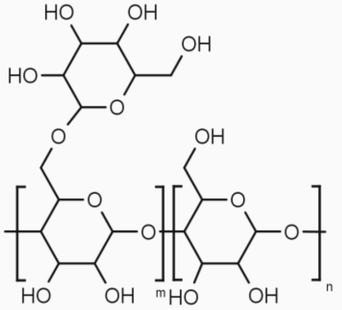
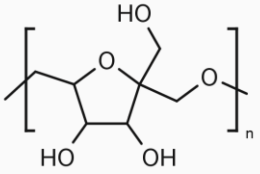
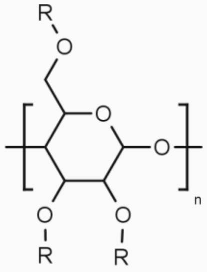
Polyalkyleneglycol (PAG)	**Polyether (PE)**	**Polyacetamide (PAC)**	**Polyacrylamide (PAM)**	**Polyalcohol-ester (PAE)**
				
“PAG1”– 400 cSt, 50%WS/50%WI “PAG2”– 1100 cSt, 60%WS/40%WI “PAG3”– 17000 cSt, 75%WS/25%WI	“PE1” – Very Low MW “PE2” – Low MW “PE3” – Medium MW “PE4” – High MW	“PAC1”–Low MW “PAC2”–Medium MW “PAC3”–High MW	“PAM1” – Very High MW	“PAE1”– Medium MW, 88%WS/12%WI “PAE2”– Medium MW, 92%WS/8%WI “PAE3”– Medium MW, 99%WS/1%WI

R and **R’** = H or CxHy functionality

“**%WS**” = mol% water soluble monomer “**%WI**” = mol% water insoluble monomer

MW (Molecular Weight): “Very Low”=< 1000; “Low”=10k-100k; “Medium”=100k-200k; “High”=300k-400k; “Very High” =1-10M

Table 3: Classes and naming key for biobased and modified biobased polymers evaluated in this study.

Linear Polysaccharide (PSL)	**Branched Polysaccharide (PSB)**	**Modified* Linear Polysaccharide (MPSL)**	**Modified** Branched Polysaccharide (MPSB)**
			

R = $C_xH_yO_z$

*= Modified by hydrolysis/isomerization ** = Modified by chemical grafting

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

Most polymers were easily dissolved in filtered water at 40-60°C / 104-140°F with stirring on a hotplate in one to two hours. PAE polymer chemistry required heating at 80-90°C / 176-194°F for several hours. Glassware was tared and any evaporated mass of water lost from start to finish was replaced. Each polymer was first prepared as concentrates at roughly 1000 cSt @ 40˚C and filtered at 10 µm before preparing ISO 22 – 680 grades. No biocides were used.

Biobased polymers (PSL and PSB) exhibited poor solubility and necessitated processing with alkali or chemical modification to prepare water-polymer blends. Details are described in **Appendix B**.

Viscosity and Viscosity Index

Kinematic viscosity was measured by Cannon-Fenske capillary viscometer (ASTM D445) at 40°C (KV40) and 80°C (KV80) for each polymer at various wt%. Since water boils at 100°C / 212°F, an effective KV100 was extrapolated from KV40 and KV80 using ASTM D341. The effective KV100 and measured KV40 were used to calculate viscosity index by ASTM D2270.

3. Results and Discussion

Viscosity from Water Soluble Polymers

Figure 5 presents the nine chemistries from **Tables 2 and 3** arranged by biodegradability and renewability ("eco-friendliness"). Not all biodegradable polymers were bio-based and vice versa. EAL programs, like Ecolabel, may stress biodegradability over renewability. Exact biodegradability will vary by MW, end groups, and application.

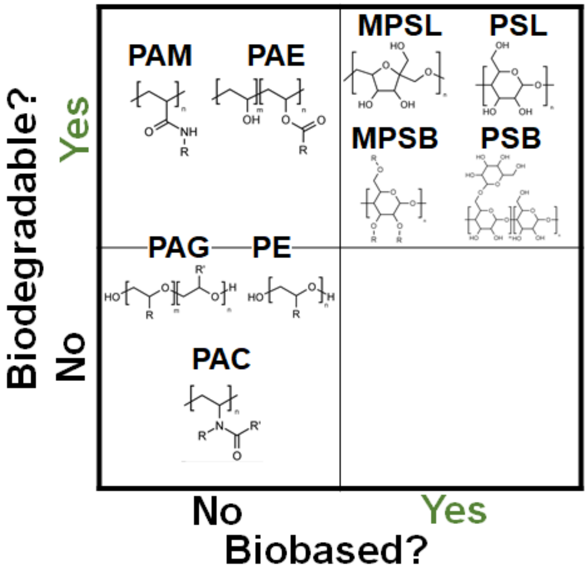


Figure 5: Water soluble chemistries by their relative "eco-friendliness" (biodegradability and renewability).[9] [30] [31] [32] [33] Biodegradability of PAG and PE chemistries are highly dependent on MW and shown 'on the fence'.

Table 4 compares the thickening rate of all synthetic/biobased polymer chemistries by the wt% required for ISO 46 and 460 with their VI. This metric was chosen over the typical "1wt% polymer in base oil" metric due to the very wide contrast in MW (10^2 to 10^7 g/mol) and the very low viscosity of water (<1 cSt). These viscosities are typical for hydraulic fluids and industrial gear oils, respectively.

Table 4: Comparison of synthetic and biobased water soluble polymer chemistries for viscosity modification.

Chemistry	Functional Groups	Polymer	MW Range	ISO 46 in H_2O		ISO 460 in H_2O	
				%polymer	VI*	%polymer	VI*
Synthetic Polymers							
PAG	Ether -O-	PAG1	Low	49-51%	sep.	N/A	sep.
		PAG2	Low	39-41%	sep.	73-77%	152
		PAG3	Low	26-27%	sep.	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 -OH Ester -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	Ether -O-, Hydroxyl -OH, Ring 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	Ether -O-, Hydroxyl -OH, Ring 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 were the least favorable at >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.

Unique Behaviors of Different Water Soluble Chemistries

PAG copolymers were tested at various ratios of water soluble to water insoluble monomer. The addition water insoluble monomer turns **PAG** in a very convenient liquid. Above 40°C, each PAG demonstrated various extents of 'phase separation' where the blends separated into two layers in **Figure 6**.

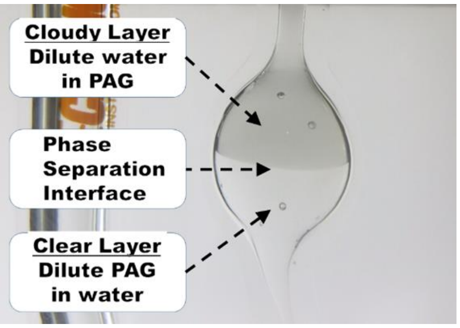


Figure 6: Phase separation of 20wt% PAG4 in water at 80°C in a capillary viscometer. Separation results in an opaque top layer (PAG) on top of a clear layer (water).

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 $\leq$ 20wt% PAG3 phase separated at 80°C but concentrations >40wt% were clear at 80°C. KV80 and VI could not be reliably obtained. This is an example of "lower critical solution temperature" (LCST) behavior where the solubility of a polymer in fluid becomes worse with temperature.[34] [35] In short, the attraction between the ether sites of water soluble monomers of PAG and H_2O that make the polymer soluble will break down when heated and leave behind only the hydrophobic attraction of the carbon-hydrogen segments between polymers.[36] [37] The hydrophobic portions associate between polymers and separate out as haze or a second layer.[38]

PE polyether blends were prepared using polymer of 100% WS monomer content. The spacing of oxygens along the PE polymer backbone coincides with the natural spacing of oxygen in water and is attributed to its good solubility.[35] Unlike PAG chemistry, all PE polymers were found to be soluble at 40°C and 80°C which allowed measurement of viscosity index. 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.

Room temperature haze of high MW PE polymers in water was reduced by 96% via the addition of complex salts and a small of amount of surfactant. The complete approach is described in **Appendix A**. 90% of haze was attributed to a weak solvent cage of water clusters around the polymer (**Figure 7a**) which allowed individual chains to form hazy aggregates. The addition of large complex ions (**Figure 7b**) strengthened the water clusters and provided a barrier between chains. This resulted in bright and clear solutions of PE polymer in water from room temperature to testing at 80°C.

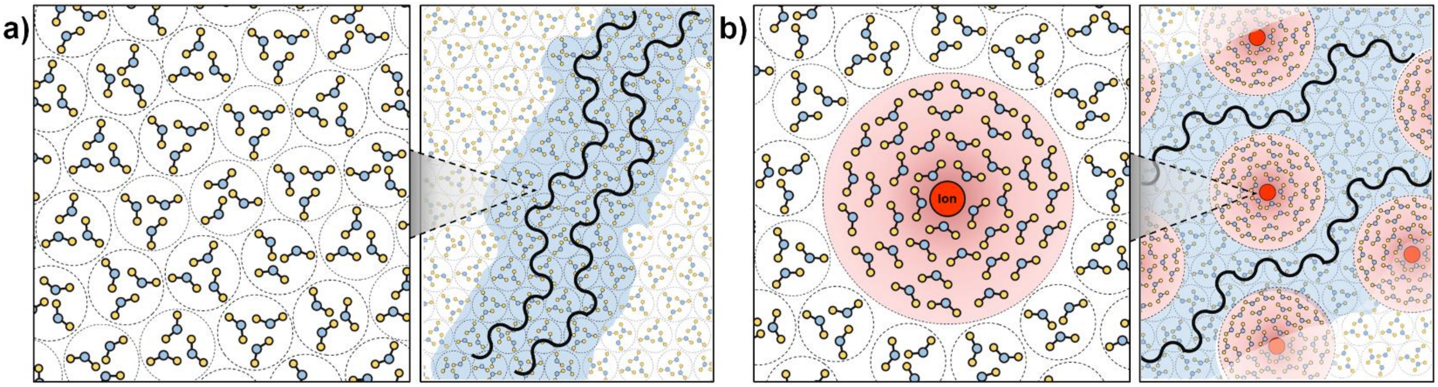


Figure 7: a) Water (*blue/yellow*) by itself makes weak solvent cages (*blue*) around PE polymer (*black lines*) that allow polymers to contact and form haze; **b)** Ions (*red*) cause water to form stronger clusters and block polymer contact.[37]

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. PAM was notably more difficult to dissolve than the PAC due in part to the higher MW but also the presence of hydrogens on the amide sites. Amide protons introduce very strong intermolecular bonds – this is the basis of extremely tough polyamide fibers.

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 8 depicts the fundamental principle behind observed differences in ease of solubilizing as well as haze and foam tendency in water soluble polymers. 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.

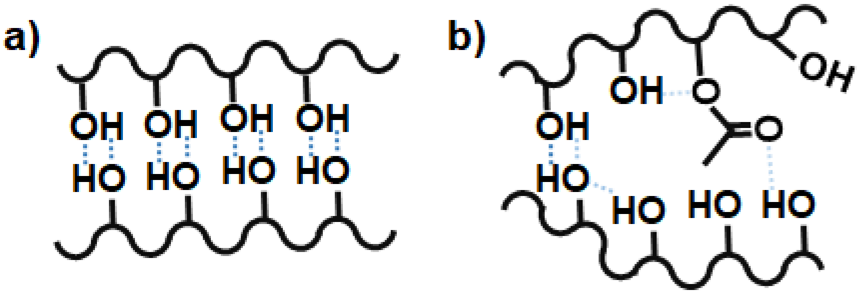


Figure 8: a) Polymers with polar/h-bonding monomers are difficult to dissolve due to the formation of extensive hydrogen bonding networks that must break down to dissolve (PAE3, PSL, PAM). b) The addition of bulky side groups (PAE1, MPSB, PAC) introduces high amounts of disorder to prevent the network from forming.

PAE chemistry was evaluated at varying alcohol/ester ratios: PAE1 = 88% hydroxyl, PAE2 = 8%, PAE3 = 1%. Each PAE polymer was derived from hydrolysis of the same 0% hydroxyl feedstock. Higher water soluble –OH content improved the thickening efficiency. The polymer interacted with more H_2O through more –OH sites and became more soluble to provide higher viscosity. However, VI improvement decreased with increasing hydroxyl content and solubility of the polymer. This corroborated a common hypothesis for VI improvement.[3] [22] If viscosity index is driven by the contraction of polymer chains at low temperature and expansion at high temperature then having a less soluble but still soluble polymer would cause the polymer to compress more at low temperature and produce a greater expansion.
The same effect is accomplished by insoluble methyl methacrylate and styrene in polymethacrylate and styrene OCP VI improvers.

PAE was also notable for is high tendency for foaming. This is likely due to hydrogen bonding between hydroxyl (-OH) groups which bind tightly and are difficult to dissolve even in water (as in **Figure 8**). PE polymers also exhibited tendency to foam but to a less extent. Since PE polymers only contain ether (-O-) linkages and do not hydrogen bond like PAE the foam was instead attributed to hydrophobic attraction between CH_2 and alkyl chain ends.

PS/MPS, biobased 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.

Performance Additives

Base fluid and polymers are used to achieve the proper viscometrics but additives are needed to make a finished industrial lubricant that properly protects and lubricants equipment. **Table 5** outlines a water-based hydraulic fluid using a water/glycol base blend and VI improver.

Table 5. Components of a basic water-based hydraulic fluid.

Component	Primary Functions	Advantage(s)	Disadvantage(s)
Water	Fire resistance, base fluid	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

Several water soluble components were evaluated at 0.5wt% for AW/EP behavior and ferrous corrosion in **Table 6** with ISO 46 polyether 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.[3] Water-based lubricants require water-soluble components. These additives are typically water-soluble sodium salts of fatty acids, sulfur/phosphorus/oxides, or sulfurized triazines.[4]

Table 6: Performance of various biodegradable surface-active components (AW/EP/CI) in ISO 46 PE-water

Formula	4-Ball Wear (D4172)	4-Ball EP Weld (D2783)	Iron Chip Corrosion (D4627)
A: ISO 46 polyether PE3 in water	1.13 mm @ 20kgf	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). 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.

Defoamers – Excessive foaming can cause cavitation, poor heat removal, and reduction in the effectiveness of performance additives.[39] A simple defoamer shake test was performed in ISO 46 solutions of PAE and PE polymer with silicone, butyl acrylate, and PAG defoamers. The PAG defoamer was the only chemistry effective at removing foam in the ISO 46 PAE and PE. Shake tests should be followed with ASTM D892 for quantification.

4. Conclusion

This work evaluated the potential of many synthetic and biobased water-soluble polymers for use in the viscosity modification of water. The goal of this paper was to begin to optimize the search for the 'right' viscosity modifier or VI improver in a potential water-based lubricant: more choices can expand the formulator's toolbox but can also add more complexity in the decision-making process.

Synthetic polymers offered the best viscosity index improvement but had varying biodegradability and moderate treat rates to meet ISO 46 and 460. Biobased polymers tend to require extra processing but yield very high MW products with excellent thickening efficiency and biodegradability. The water-soluble polymers studied tended to be renewable and/or biodegradable which would be ideal for environmentally acceptable lubricants (EAL) in applications like forestry, maritime, oil exploration, and other sensitive industries.

Future work will entail the measurement of polymer shear stabilities so that shear stable aqueous lubricants may be formulated. Unlike petrochemical lubricants an exceptionally high fraction of the viscosity in a water-based lubricant must be added by shearable polymers. Meeting that challenge and establishing which additives to use for AW/EP/CI roles would be key to proceeding with the fully formulated industrial lubricants.

Appendix A: Clarifying Polyether Blends in Water

Two major features of PE polymer dissolved in water are attributed to haze: a weak solvent cage and, discussed later, clustering of end groups. By understanding these effects one may hope to modify their behavior.[40]

The *first feature* is the formation of a solvent 'cage' or 'shell' structure.[38] 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.

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'.[37] [41] 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 (**Figure 7a**, in Discussion).[37] 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 (**Figure 7b**, in Discussion). These interactions orient and polarize the clusters of water into well-defined layers of structure surrounding the ionic core.[35] [37] Large multiply charged anions, or polar species like OH^- and F^- improve cloud point by up to 40°C.[38]

Cloud point modification was studied in an ISO 15 blend of PE3 polymer in water. A relatively dilute solution was chosen to avoid concentration effects. Progress in eliminating haze was measured at room temperature by turbidity meter in Formazin Nephelometric Units (FNU) using a Milwaukee Mi 415 portable turbidity meter (**Figure 8**). FNU turbidity quantifies the amount of infrared light scattered by haze in solution from a 90 degree angle. The instrument was calibrated with aqueous standards of 0, 10, and 500 FNU.

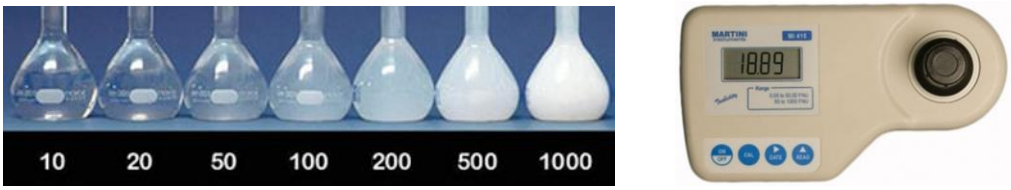


Figure 8: Turbidity in FNU from 10 – 1000 units (modified from Optek.com) with turbidity meter on right. < 20 FNU is ideal for high clarity products while 30 - 50 units is detectable to the eye as slight haze. Haze usually undesirable.

The ISO 15 formulation exhibited an initial 246 FNU haze and was nearly opaque. Sodium and calcium acetate were tested by adding 1 mole per liter (1M) based on literature.[38] These salts produced no effect on haze. A high MW inorganic salt was tested next and produced a significant decrease in haze upon cooling. This salt possessed the same feature of so-called 'structure maker' salts in literature.[37] [38] This compound will be referred to as "clarifier salt".

Clarifier salt treat rate was varied to find an optimal treat in the ISO 15 solution. **Figure 9** compares haze from the 'no salt' control (246 FNU) to an idealized ratio of 0.5 (1 part salt to 2 parts polymer) of 24.1 FNU. Above a ratio of 2.5 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 concentration was well in excess of the ideal 0.5 ratio.

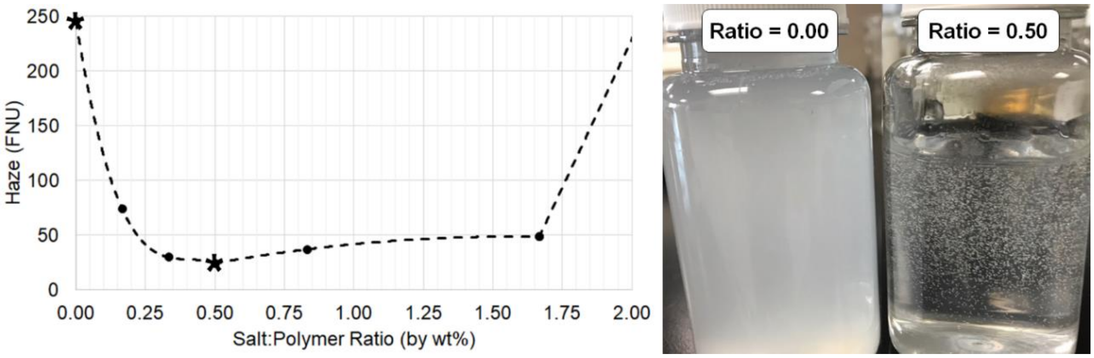


Figure 9: Measured haze in ISO 15 solution versus polymer: salt added. The use of large complex ions reinforces the solvent cage and screens polymer aggregation to allow PE-water blends as clear liquid VI improver.

This salt strategy reduced, but did not eliminate, visible haze in ISO 15 by 90% from 246 to 24.1 FNU. Yet 20 FNU or greater would be considered slightly haze to an observer. The remaining 10% haze must arise from to a second cause.

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.[40] 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.[40] This effect can be reduced if a bifunctional diol initiator (i.e. ethylene glycol) is used.

It was hypothesized that if this hydrophobic interaction of the alkyl end group could be fulfilled by small molecule co-solvents or surfactants rather than end group-to-polymer associations then clustering would cease and additional reduction in haze would occur. Initial C3 to C6 glycols were tested at 5-20wt% but failed to affect haze. High MW glycols tended to affect solubility and add haze before any reduction was observed.

It was rationalized that the compatibilizer needs a larger hydrophobic segment to associate with the alkyl chain ends while also being highly soluble in water. The need for a single compound with two starkly different types of solubility led to using surfactants. The chain end was envisioned as a species which needs to be emulsified into water with an appropriate surfactant, ideally as a clear micro-emulsion. Testing began with a small (0.5wt%) treat of sorbate esters.

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 10** 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.

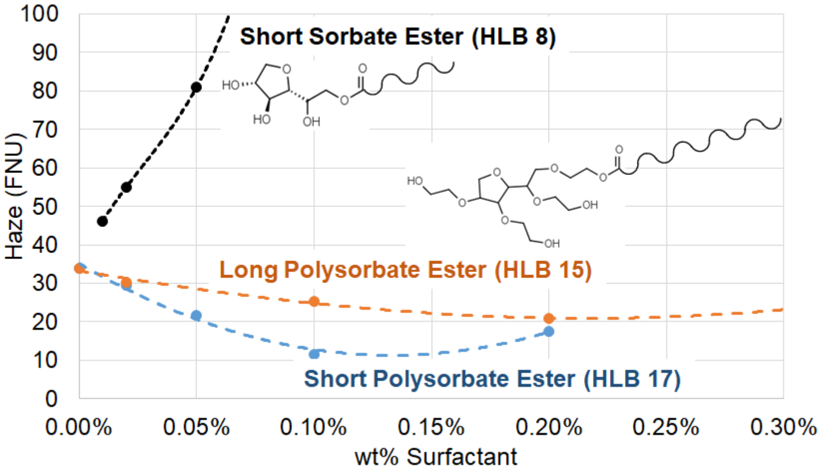


Figure 10: Measured haze in ISO 15 polyether-water formulations with clarifier salt versus treat rate of three sorbate-based surfactants to aid in dispersing hydrophobic chain ends. The short chain polysorbate was the most hydrophilic of the three and best suited to further reducing the haze.

Long sorbate ester failed condition 1 since it was an insoluble wax. Short sorbate ester failed condition 2 as it added considerable haze even at low < 0.10wt% treat. Testing even lower HLB surfactants required the polysorbates. Both long and short polysorbates were effective in continuing to reduce haze from the 24.1 FNU with clarifier salt. Long polysorbate ester gave a minimum of 20 FNU at 0.25wt%. Short polysorbate ester gave 10 FNU at about 0.12wt%. These values ($\leq$ 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’ clarifier salt and short polysorbate surfactant reduced haze to by 96% to 11.6 FNU and fulfilled the goal of making water-white (< 20 FNU) polyether-water 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: Preparation of More Soluble Polysaccharides

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.[42] High biodegradability and renewability from biobased 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.[43] 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 linear vs. branched biobased polysaccharides, their solubility, and how to better process these materials for water-based lubricants using chemical modification.

Processing the polysaccharides 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.[44] [45] **Figure 11** 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.

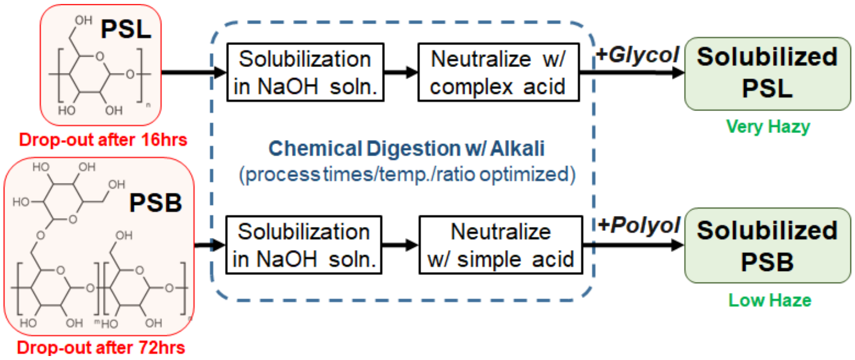


Figure 11: Workflow for solubilizing of PSL and PSB to more soluble and stable water-based thickeners with high bio-based content and thickening efficiencies. Haze remains but is treated by adding an appropriate co-solvent.

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.[46] [47]

Figure 12 outlines the chemical modification of biobased polysaccharides to produce MPSL and MPSB polymers.[43] 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.[48] [49]

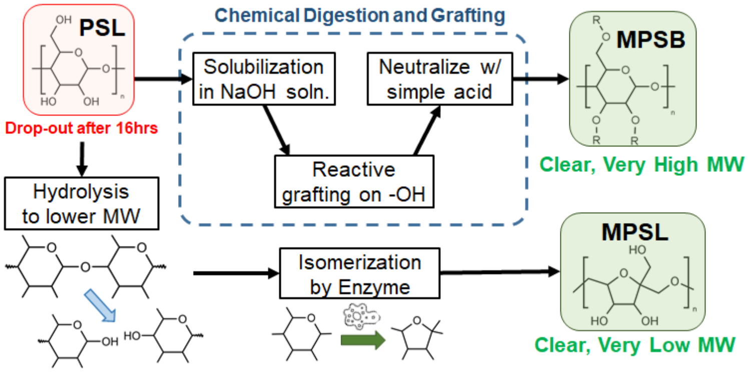


Figure 12: Workflow for chemical modification of polysaccharides to obtain thickeners with high efficiency and exceptional clarity in water. Graft in alkali solution retains the very high MW while isomerization reduces MW.

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.[49] 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.[50] 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.

References

1. Eachus, A. C. The trouble with water. *Tribology & Lubrication Technology* 32–38 (2005).
2. Leckner, J. *Water + Grease = Fatal Attraction?* (2013).
3. Rudnick, L. R. *Lubricant Additives: Chemistry and Applications, Second Edition*. (CRC Press, 2009).
4. Totten, G. E. *Handbook of Hydraulic Fluid Technology*. (Taylor & Francis, 1999).
5. Pfadt, M., Wiesbock, M., El Allam, S. & Kuhn, M. Hydro Lubrication: The Future of Lubricants is Based on Water. in *Technische Akademie Esslingen - 21st International Colloquium Tribology* 21–22 (2018).
6. EU Ecolabel Lubricants / Industrial and marine gear oils. (2018). Available at: http://ec.europa.eu/ecat/category/en/51/industrial-and-marine-gea. (Accessed: 13th November 2018)
7. Canter, N. Growth likely but future still uncertain for environmentally friendly additives. *Tribology & Lubrication Technology* 12–22 (2018).
8. Mortier, R. M., Fox, M. F. & Orszulik, S. T. *Chemistry and Technology of Lubricants*. (Springer Netherlands, 2011).
9. Vroman, I. & Tighzert, L. Biodegradable Polymers. *Materials (Basel).* **2**, 307–344 (2009).
10. Das, N. & Chandran, P. Microbial degradation of petroleum hydrocarbon contaminants: an overview. *Biotechnol. Res. Int.* **2011**, (2011).
11. *European Union Ecolabel application pack for lubricants: Version 1.1 – September 2014*. (2014).
12. European Union Ecolabel - COMMISSION DECISION of establishing the EU Ecolabel criteria for lubricants.
13. ASTM. *Fuels and Lubricants Handbook*. (2003).
14. Kuchta, J.M.; Cato, R. J. Review of Ignition and Flammability Properties of Lubricants. *Air Force Aero Propuls. Lab.* (1968).
15. Wrenick, S., Sutor, P., Pangilinan, H. & Schwarz, E. . Heat Transfer Properties of Engine Oils. *World Tribol. Congr. III* 1–2 (2005). doi:10.1115/WTC2005-64316
16. Medved, T.M.; Bolze, C.C.; Hansen, C.E.; Borger, A. W. Heat Capacity Determination of Mineral and Synthetic Engine Oils, Lubricants, Fuels, and Hydraulic Fluids. *Wright Air Dev. Cent.* (1959).
17. Schwingel, W.R.; Eachus, A. C. Chapter 15: Antimicrobial Additives for Metalworking Lubricants. in *Lubricant Additives: Chemistry and Applications, Second Edition* 383–398 (2009).
18. Passman, F. J. The Path Ahead for Metalworking Fluid Microbiology. *Lubes N' Greases* 44–48 (2018).
19. Water Industry Still Striving to Articulate Resource's Value. *Environ. Bus. J.* **XXIII**, (2010).
20. STLE. *Trends in Tribology and Lubrication Engineering: 2014 Report on Emerging Issues and Trends*. (2014).
21. Wang, S. & DeVore, D. A study of polymer additives in mineral oil and vegetable oil-based greases. *ELGI 2011* (2011).
22. Willett, Erik; DeVore, Andrew; Vargo, D. Viscometric and Low Temperature Behavior of Lubricants with Blended VI Improvers. *Funct. Prod. Inc.* (2017).
23. Storer, F. H. *First outlines of a dictionary of solubilities of chemical substances*. (1864).
24. Miller-Chou, B. A. & Koenig, J. L. A review of polymer dissolution. *Prog. Polym. Sci.* **28**, 1223–1270 (2003).
25. Hildebrand, J. H. A critique of the theory of solubility of non-electrolytes. *Chem. Rev.* **44**, 37–45 (1949).
26. Griffin, W. C. Classification of surface-active agents by" HLB". *J. Soc. Cosmet. Chem.* **1**, 311–326 (1949).
27. ICI Americas, inc. *The HLB System: A Time-saving Guide to Emulsifier Selection*. (ICI Americas, Incorporated, 1984).
28. Hansen, C. M. *Hansen Solubility Parameters: A User's Handbook, Second Edition*. (Taylor & Francis, 2007).
29. Krevelen, D. W. Van. *Properties of Polymers: Their Estimation and Correlation with Chemical Structure*. (Elsevier, 1976).
30. Beran, E., Hull, S. & Steininger, M. The Relationship Between the Chemical Structure of Poly(alkylene glycol)s and Their Aerobic Biodegradability in an Aqueous Environment. *J. Polym. Environ.* **21**, 172–180 (2013).
31. Kawai, F. Biodegradation of Polyethers (Polyethylene Glycol, Polypropylene Glycol, Polytetramethylene glycol, and Others). *Biopolymers Online* (2005). doi:doi:10.1002/3527600035.bpol9012
32. Joshi, S. J. & Abed, R. M. M. Biodegradation of Polyacrylamide and Its Derivatives. *Environ. Process.* **4**, 463–476 (2017).
33. Azahari, N. A., Othman, N. & Ismail, H. Biodegradation studies of polyvinyl alcohol/corn starch blend films in solid and solution media. *J. Phys. Sci.* **22**, 15–31 (2011).
34. Saeki, S., Kuwahara, N., Nakata, M. & Kaneko, M. Upper and lower critical solution temperatures in poly (ethylene glycol) solutions. *Polymer (Guildf).* **17**, 685–689 (1976).
35. Kjellander, R. & Florin, E. Water structure and changes in thermal stability of the system poly(ethylene oxide)–water. *J. Chem. Soc. Faraday Trans. 1 Phys. Chem. Condens. Phases* **77**, 2053–2077 (1981).
36. Rubinstein, M. Chapter 4: Thermodynamics of mixing. in *Polymer Physics* 137–170 (2003).
37. Frank, H. S. & Wen, W.-Y. Ion-solvent interaction. Structural aspects of ion-solvent interaction in aqueous solutions: a suggested picture of water structure. *Discuss. Faraday Soc.* **24**, 133–140 (1957).
38. Ataman, M. Properties of aqueous salt solutions of poly(ethylene oxide). Cloud points, θ temperatures. *Colloid Polym. Sci.* **265**, 19–25 (1987).
39. Gresham, R. M. What's so bad about foamy foams? *Tribology & Lubrication Technology* 22–23 (2018).
40. Hammouda, B., Ho, D. L. & Kline, S. Insight into Clustering in Poly(ethylene oxide) Solutions. *Macromolecules* **37**, 6932–6937 (2004).
41. Israelachvili, J. & Wennerström, H. Role of hydration and water structure in biological and colloidal interactions. *Nature* **379**, 219 (1996).
42. Saha, D. & Bhattacharya, S. Hydrocolloids as thickening and gelling agents in food: a critical review. *J. Food Sci. Technol.* **47**, 587–597 (2010).
43. Kostag, M., Jedvert, K., Achtel, C., Heinze, T. & El Seoud, O. A. Recent advances in solvents for the dissolution, shaping and derivatization of cellulose: Quaternary ammonium electrolytes and their solutions in water and molecular solvents. *Molecules* **23**, (2018).
44. Zhang, L., Ruan, D. & Gao, S. Dissolution and regeneration of cellulose in NaOH/Thiourea aqueous solution. *J. Polym. Sci. Part B Polym. Phys.* **40**, 1521–1529 (2002).
45. Budtova, T. & Navard, P. Cellulose in NaOH – water based solvents : a review. **23**, 5–55 (2017).
46. Scotchman, I. C. Shale gas and fracking: exploration for unconventional hydrocarbons. *Proc. Geol. Assoc.* **127**, 535–551 (2016).
47. Pangilinan, K. D., de Leon, A. C. C. & Advincula, R. C. Polymers for proppants used in hydraulic fracturing. *J. Pet. Sci. Eng.* **145**, 154–160 (2016).
48. Cumpstey, I. Chemical modification of polysaccharides. *ISRN Org. Chem.* (2013).
49. Hanover, L. Mark; White, J. S. Manufacturing, composition, and applications of fructose. *Am. J. Clin. Nutr.* **58**, 724–732 (1993).
50. Odian, G. G. *Principles of polymerization*. (Wiley, 1981).