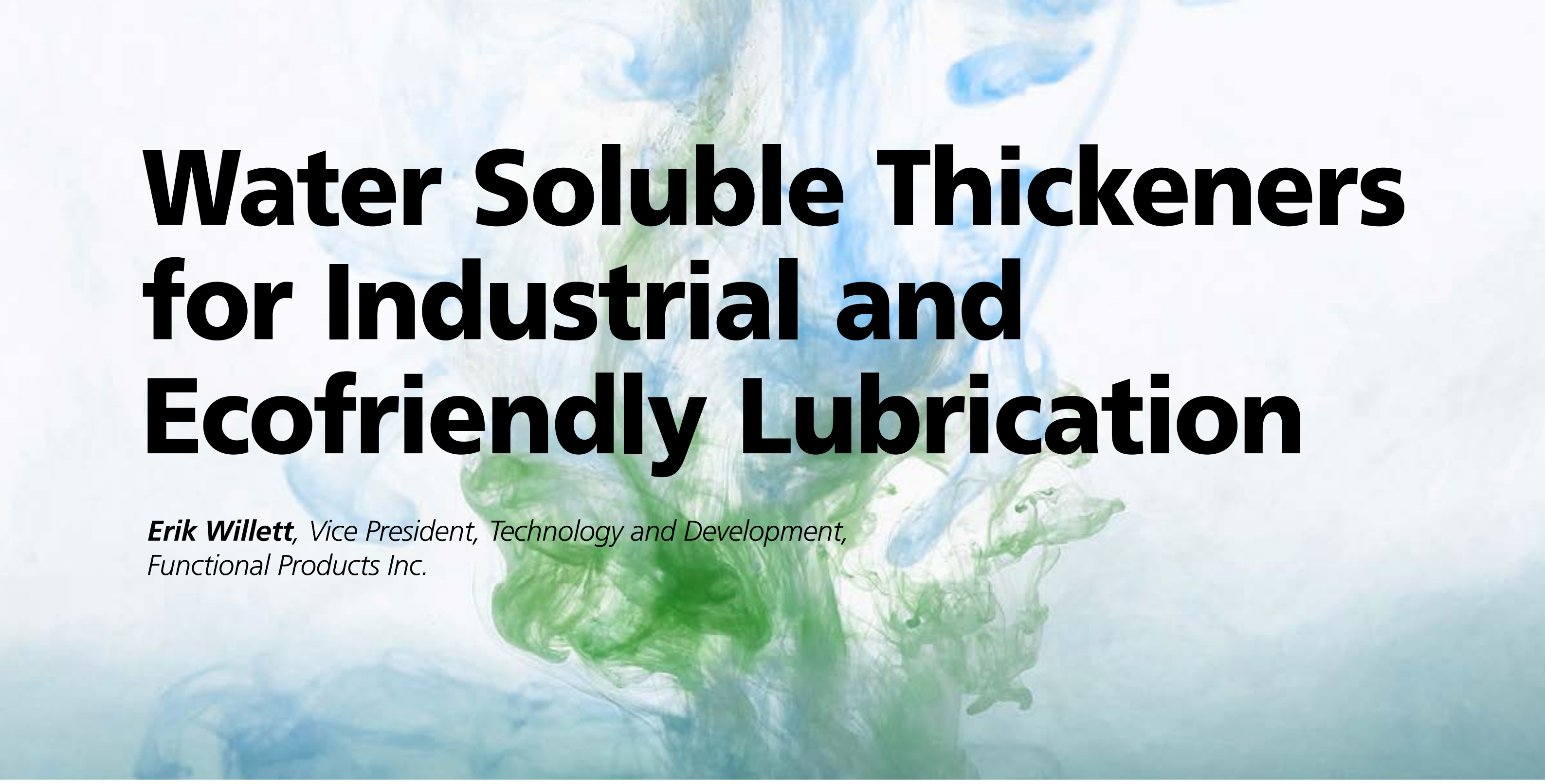

Water Soluble Thickeners for Industrial and Ecofriendly Lubrication

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Introduction

Water's role either as acomponent 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 utilise 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]

A key challenge in environmentally acceptable lubricants remains in the need to possess both the oxidative stability and high viscosity index (VI) of waxy saturated fatty acid groups but also the low temperature behaviour of unsaturates.[6] 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.[7] 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.[8] Degradation occurs by gradual breakage of polar bonds which revert the polymer to oligomers and finally monomers.[8] C-C bonds can degrade if the molecule is small and soluble.[9]

The accumulation of synthetic materials on land and at sea has become an increasing concern. Environmentally acceptable lubricant (EAL) programmes like European Ecolabel outline specifications for biodegradability and renewability in lubricants to be used in sensitive applications like maritime and forestry. [10] [6] 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.

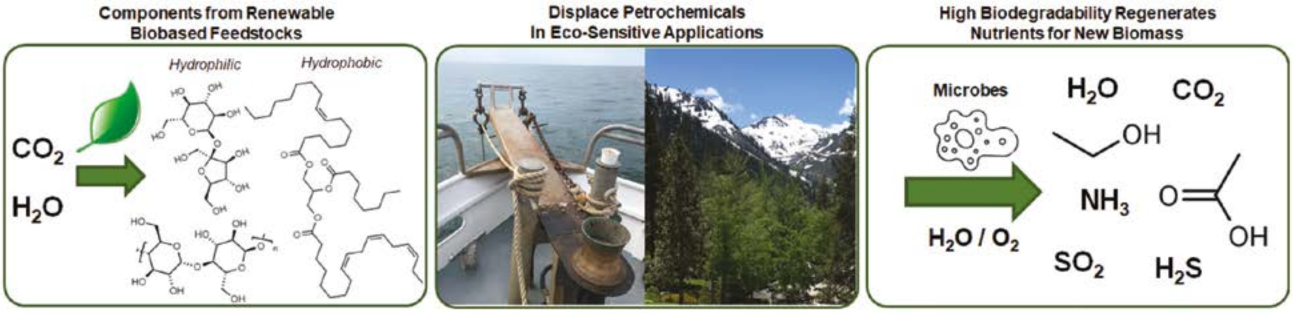


Figure 1: *Lifecycle of environmentally acceptable lubricants (EAL) from renewable beginning to biodegradable ending*

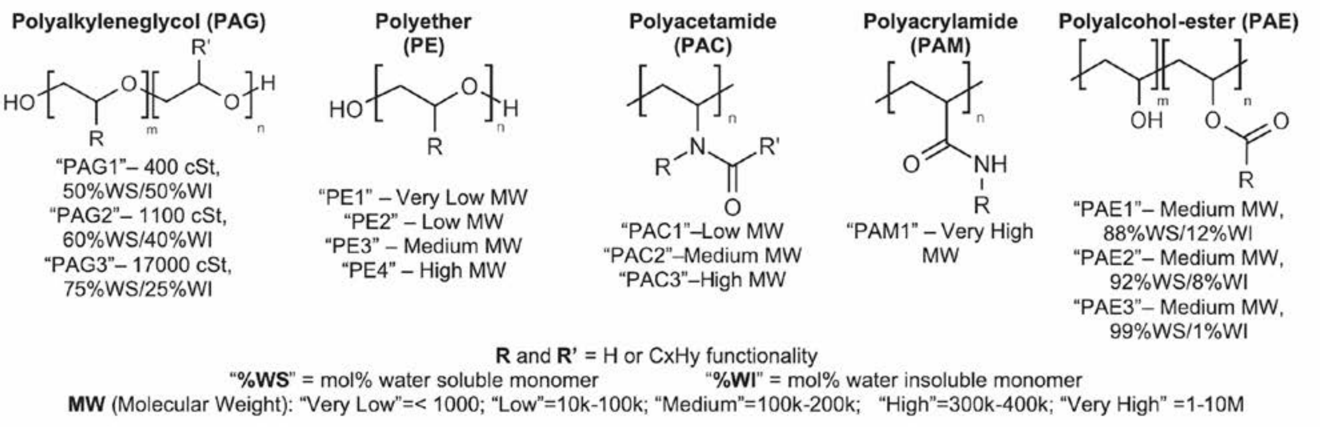


Table 2: *Chemistries and naming key for various grades of synthetic polymers evaluated in this study*

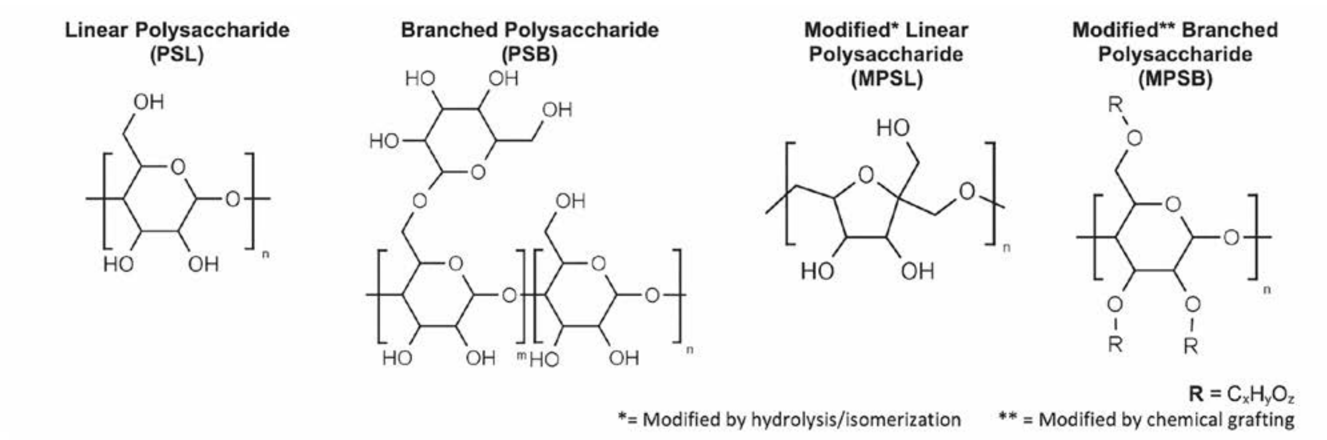


Table 3: *Classes and naming key for biobased and modified biobased polymers evaluated in this study*

Synthetic and Biobased 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 molecular weight and chemical identity are proprietary.

Sample Preparation and Methods

Within one to two hours, most polymers were easily dissolved in filtered tap water at 40-60°C / 104-140°F with stirring on a hotplate. Poly(aryleneethynylene)s (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 at 40˚C and filtered at 10 μm before preparing ISO 22 – 680 grades. No biocidal stabilisers were added.

Biobased polymers (PSL and PSB) exhibited poor solubility and necessitated processing with alkali or chemical modification to prepare water-polymer blends. This process has been described elsewhere.

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.

Excessive foaming was observed when handling PAE and Polyethylene (PE) chemistries. Foam can cause cavitation, poor heat removal, and reduction in the effectiveness of performance additives.[13] 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 in this screening test.

Viscometrics of 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 programmes, like Ecolabel, may stress biodegradability over renewability. Exact biodegradability will vary by MW, end groups, and application.

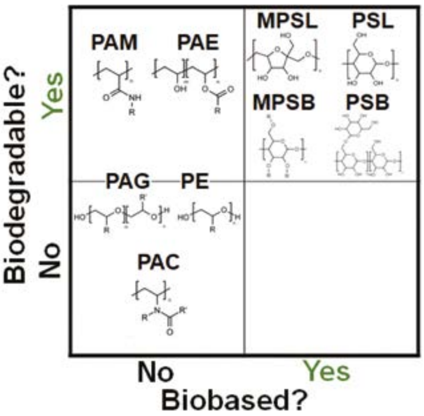


Figure 5: *Water soluble chemistries by their relative "eco-friendliness" (biodegradability and renewability).[8] [14] [15] [16] [17] Biodegradability of PAG and PE chemistries are highly dependent on MW and shown 'on the fence'.*

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 (102 to 107 g/mol) and the very low viscosity of water (<1 cSt). These viscosities are typical for hydraulic fluids and industrial gear oils, respectively.

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 Behaviours of Water Soluble Polymers

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.

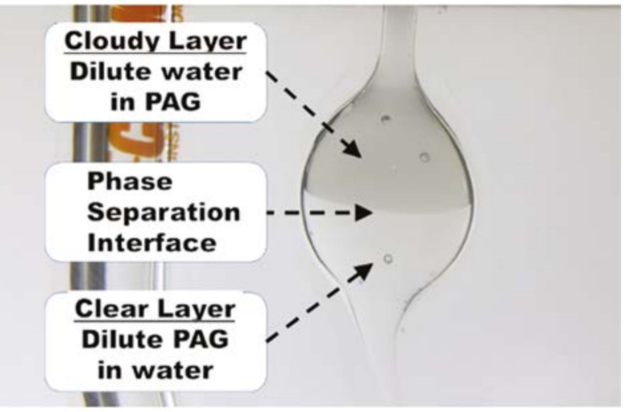
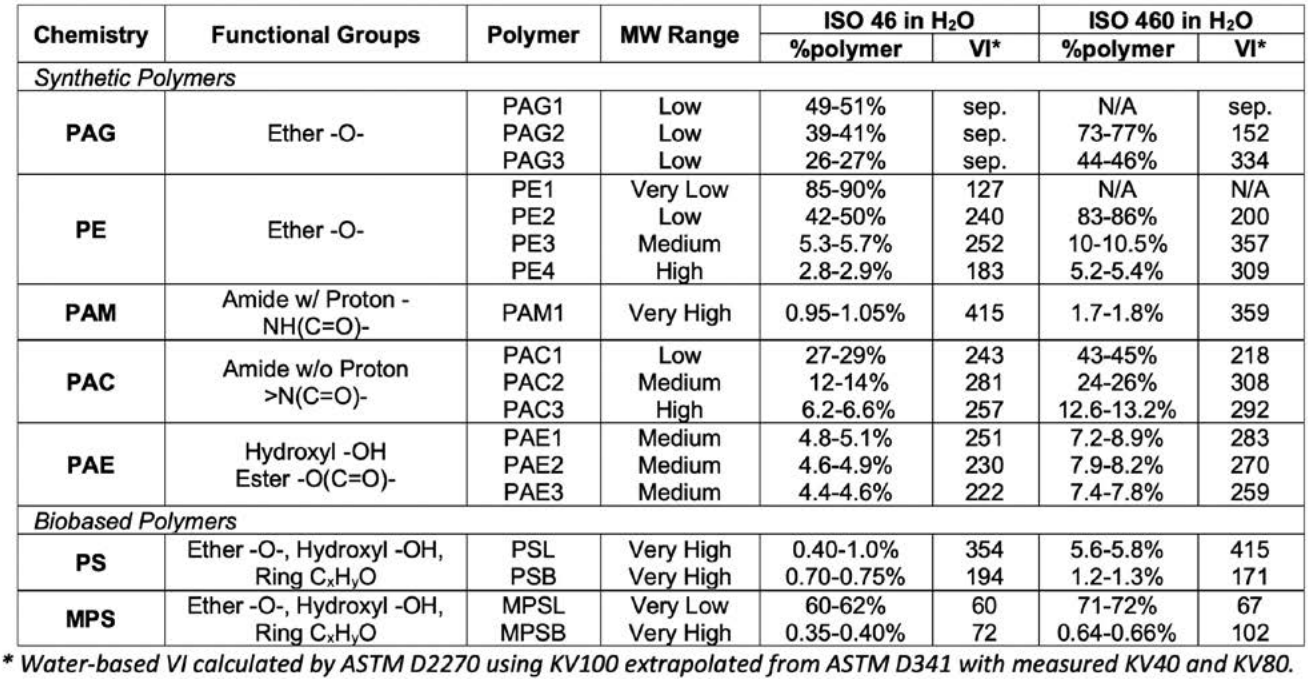


Figure 6: *Phase separation of 20wt% PAG4 in water at 80°C in a capillary viscometer. Separation results in an opaque top layer (PAG) on top of a clear layer (water)*



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.***

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

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. KV80 and VI could not be reliably obtained. This is an example of "lower critical solution temperature" (LCST) behaviour where the solubility of a polymer in fluid becomes worse with temperature.[18] [19] 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.[20] [21] The hydrophobic portions associate between polymers and separate out as haze or a second layer.[22]

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.[19] 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 polymerisation of alkylene oxide initiated by an alcohol which results in a less soluble alkyl end group.

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 fibres.

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

Figure 8 depicts the fundamental principle behind observed differences in ease of solubilising 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.

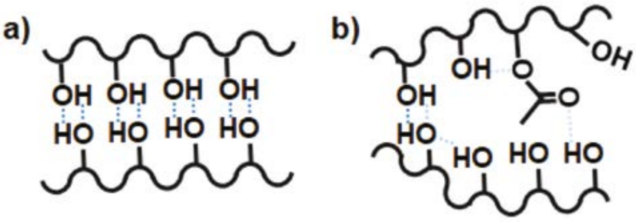


Figure 8: *Polymers with polar/h-bonding monomers are difficult to dissolve due to the formation of extensive hydrogen bonding networks that must break down to dissolve (PAE3, PSL, PAM). b) The addition of bulky side groups (PAE1, MPSB, PAC) introduces high amounts of disorder to prevent the network 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] [23] 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 its 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 lesser 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 polysaccharides required chemical transformation into new polymers, MPS, or dissolution with caustic and neutralisation to prepare stable aqueous solutions. 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 isomerisation in MPSL and grafting of water soluble groups onto MPSB provided clear and stable water-based solutions from ISO 22 – 680.

Conclusions

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 optimise the search for the ‘right’ viscosity modifier or VI improver in a potential water-based lubricant. 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 programme 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]

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.

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