The Mechanical Stability of Polymer-Modified Greases

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Abstract

Polymer additives are routinely used to improve the water resistance, oil bleed, and tackiness of grease. The role of those grease polymers in the 'mechanical stability' of grease is less known.

Mechanical stability is a broad concept but generally refers to the ability of a grease to resist changes in consistency from continued mechanical shearing in the field or by lab methods like worked cone (ASTM D217) and roll stability (ASTM D1831). Data points collected over the years does indicate that certain polymers reduce consistency losses in ASTM D217 and ASTM D1831.

This study seeks to establish a more fundamental understanding of why grease polymer structure influences the mechanical properties of grease and how to select the right grease polymer for a given grease. The study includes various polymer chemistries in combination with NLGI #2 base greases of simple lithium, lithium complex, calcium sulfonate, aluminum complex, silica, and bentonite.

1. Introduction

Preliminary Studies

The evidence presented in conferences and customer development over the decade shows that polymers affect the mechanical stability of grease. Until now, an overarching study has not been established.

Prior work in 2011 has shown that grease polymers are active in worked cone penetration.[1] A simple lithium grease (NLGI #1.5) demonstrated a +8.1% increase in cone penetration with 10,000 strokes ASTM D217. Addition of various olefin copolymers for grease reduced the change to +0.6% to +3.0% and therefore improved mechanical stability. Grease polymers were used in both solid (100% polymer) and liquid (5-10wt% polymer in 100N oil) form.

However in other cases grease polymers have provided negligible or negative changes to mechanical stability. Inorganic greases like silica and clay were shown to lose both consistency and some measure of water resistance (D4049 spray-off and D1204 wash-out) with the addition of various polymers.[2] However, two of four polymers tested in clay grease did improve D4049 spray-off which is considered to be a test of mechanical stability as well as static water resistance.

The question remains how do polymers interact with grease and why are certain greases so selective toward different polymer chemistries.

Grease Thickener Structures and Networks

Grease chemistry is highly varied but all thickener chemistries achieve the same goal, an immobilized network structure. The individual chemistry then defines the types of forces holding the network together, how those forces create a structure, and what unique properties emerge from that structure (texture, thermal/mechanical/water stabilities, etc.). **Figures 1**, **2**, and **3** demonstrate the hierarchy of structure from single molecules to grease thickener network.

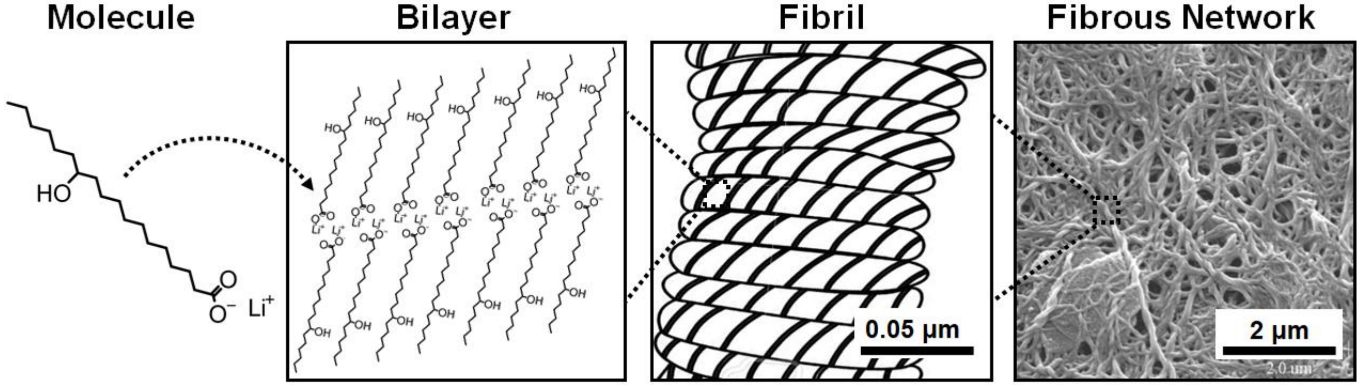


Figure 1. Fibrous grease structure (simple lithium, lithium complex). Bilayer based on [3][4][5]; microscopy from Kay[6].

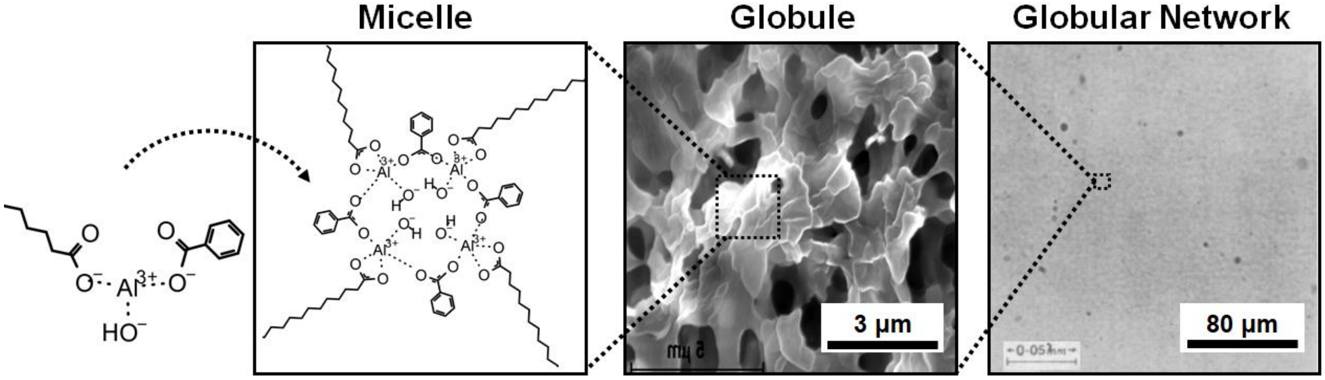


Figure 2. Globular greases structure (calcium sulfonate, aluminum complex). Micelle based on [7][8][9]; microscopy from aluminum stearates from [10][11].

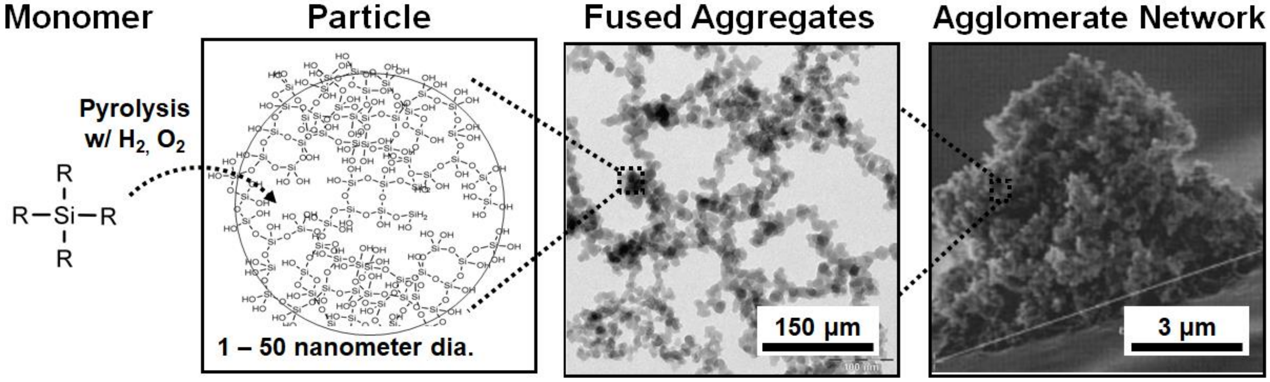


Figure 3. Particulate greases structure (silica, clay). Structures and microscopy from [12][13].

Grease Polymer Networks and “IPN” Theory

Polymers that are effective in improving the properties of grease at large (“grease polymers”) typically form rigid networks much like soaps in petroleum oil. This structuring can occur inside a grease soap network and form an “interpenetrating network” or IPN. **Figure 4** demonstrates the IPN formation process between grease soap (orange) and polymer (blue). VI improvers for lube oil are typically highly amorphous and often make poor grease polymers.

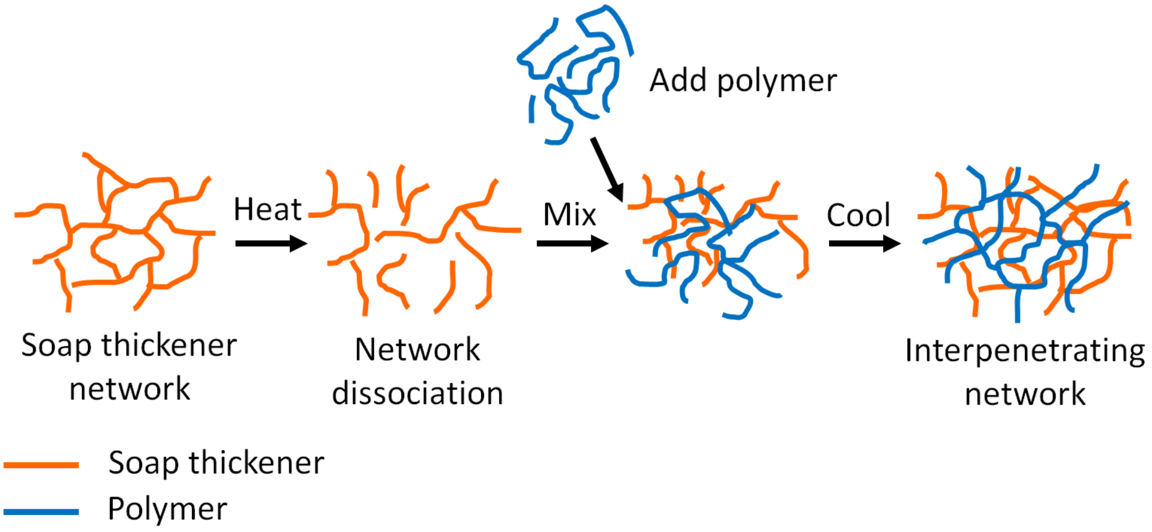
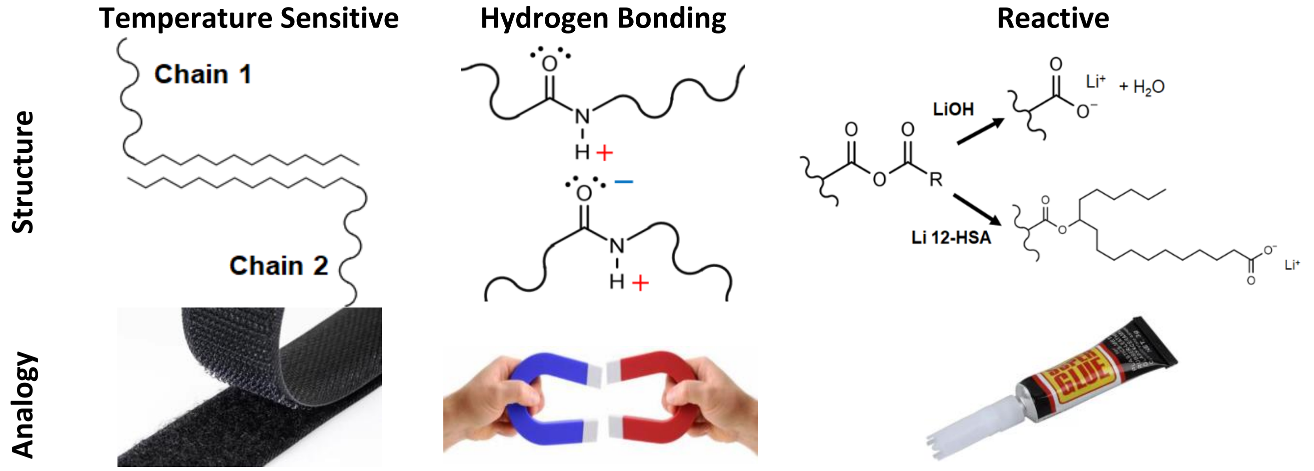


Figure 4: Formation of the interpenetrating network of polymer in grease

To be effective, the grease polymer must achieve a stable and rigid polymer network through one of three common mechanisms shown in **Figure 5** [1]:

1. **Temperature Sensitive** – long uninterrupted runs of one monomer (ethylene, styrene, etc.) along the backbone of the polymer form waxy crystallites between chains
2. **Hydrogen Bonding** – polar nitrogen and oxygen sites on the polymer separate from the non-polar oil and associate together in an acid-base attraction
3. **Reactive** – acid anhydride sites on the polymer react with metal ions to form insoluble coordination complexes (like diacids) or react with –OH sites to form covalent bonds in the thickener (like boron esters)



Hook-and-loop tape

Strong attraction

Super glue

Figure 5: Comparison of the three main mechanisms for IPN formation by grease polymers and an analogy to help remember how each one works

While formation of the IPN network of grease and polymer is generally understood to be beneficial, there are many cases where networks can be inhibited by interactions with other networks or additives. It is well-known in the field that combining two or more grease types can cause a failure of the resulting blend.[14] In this case two fully formed networks combine to form something less than the sum of their parts. Pour point depressants are polymers with long chain waxy segments that actively prevent with the formation of orderly wax networks, or gel, in low temperature lubricants.

Whether or not the IPN strategy works between any given grease thickener and grease polymer has yet to be explored in detail. This study will provide an array of different grease/polymer combinations and rationalize qualitative trends in the findings.

The goal of this work is to demonstrate, in the case of a handful of sample greases, that careful grease polymer selection matters and not to definitively show which grease polymers should be used with each grease thickener. A formulator's success in modifying grease with polymer will depend on the formulation as a whole – including base oil, complexing agents, additive packages, and production methods.

2. Experimental

2.1. Materials

Base Greases

Table 1 compares the six base greases from NLGI grade 0 to 3 were obtained with different thickener chemistries from manufacturers "A" – "E" utilized in this study.

Thickener / Name	Cone Pene. (D217)	NLGI Grade (D1403)	Base Oil (D445, D2270)	Dropping Point (D2265)	Roll Stability (D1831)	Manu.
Simple Lithium	272	2	ISO 150 VI 98	391F / 199C	+1.2%	A
Lithium Complex	264	2.5	600N VI 113	518F / 270C	+36.1%	A
Calcium Sulfonate	242	3	ISO 100 VI 111	>752F / 400C	+3.1%	B
Aluminum Complex	253	2.5	ISO 150 VI 108	542F / 283C	+1.5%	C
Silica	309	1.5	600N VI 124	642F / 339C	+2.3%	D
Clay (Bentonite)	350	0.5	ISO 460 VI 101	>752F / 400C	+11.3%	E

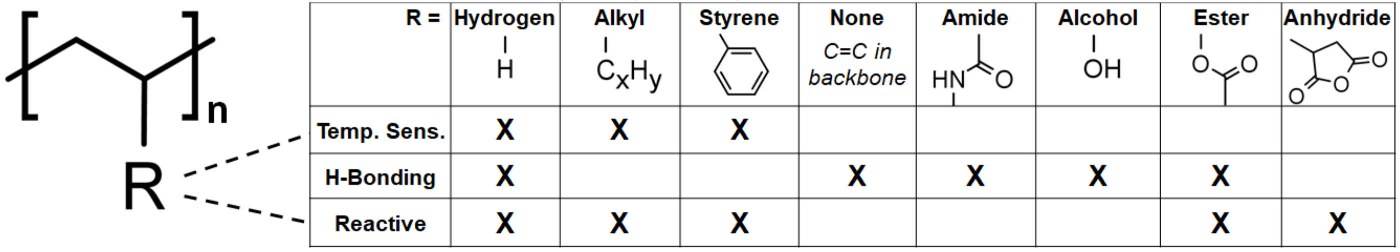
Table 1. Basic properties of the six base greases

Each grease was referenced in this study by the thickener chemistry. Base greases were formulated using typical performance additives for multi-purpose industrial grease minus any grease polymers. Base oil from each grease was obtained from oil bleed under mild conditions.[15] All six greases exhibited viscosities from ISO 100 to 460. Based on a VI range of 98 – 124, all greases were made with heavy paraffinic oils, likely Group II.

Polymers

A total of nine polymers were added individually to the six greases.

Two polymers each, a low MW (Mw 100K-200K) and high MW (Mw=300K-600K) version, were selected from each of the three grease polymer categories explained previously.[1] The exact composition of each grease polymer is proprietary but the typical functional groups are described in **Figure 6**. Performance of the polymer will vary based on the number and ratio of these monomers, the molecular weight, crystallinity, and other structural factors.



R =	Hydrogen H	Alkyl C_xH_y	Styrene	None C=C in backbone	Amide	Alcohol OH	Ester	Anhydride
Temp. Sens.	X	X	X					
H-Bonding	X			X	X	X	X	
Reactive	X	X	X				X	X

Figure 6: Typical functionality of the three grease polymer mechanisms

Additionally, two tackifiers of low MW (Mw 500K-1M, OCP) and high MW (Mw 4M-6M, PIB) were included due to their ability to form entangled networks in lube and grease. A dispersant polymethacrylate was also included due to its high hydrogen bonding capability and to cover recent interest in PMA in grease.

2.2. Methods

Polymer Solution Preparation

Polymers were pre-dissolved at 8-10wt% in 100N Group II oil to allow consistent and high-throughput blending of different polymers into the base greases. Grease polymers were solubilized for 24 hours at 100-120°C and filtered at 150 micron before adding hot to grease. 0.1wt% BHT was included.

Polymer Modified Grease Preparation

Base greases were top-treated with 5 parts polymer solution to 95 parts grease and mixed on low speed at 80-100°C for 2 hours. Base greases were milled during initial production and not milled again after adding liquid form polymer. Greases were left to rest at 20-25°C for 24 hours before testing.

Consistency Measurement and Cone Penetration

All cone penetrations reported in this study are 60 double-stroke worked penetrations converted from quarter-scale measurement and reported in mm/10 (ASTM D1403; Precision Scientific Co. #D-5). NLGI grade was assigned by ASTM D217 with half grades: "0.5", "1.5", etc. Extra care was taken to remove voids in tacky samples before testing.

ASTM D1831 Roll Stability

ASTM D1381 roll stability was used to quantify mechanical stability at an outside ISO 17025-2017 laboratory. Standard conditions (2hrs, 25°C) with ¼ cone penetrations were used. Roll stability was reported as the percent change in initial consistency vs. sheared consistency. A positive percentage ("+1%") means penetration increased and the grease has softened, i.e. from 300 to 303. Negative ("-1%") means penetration decreased and grease thickened.

3. Results and Discussion

3.1 Changes in Grease Consistency with Polymer

Before evaluating changes to grease's consistency with mechanical shearing, it is important to understand the contribution an added grease polymer can make to the grease's consistency pre-shearing. A basic grease uses heavy oil and thickener to achieve the desired NLGI grade. Thickener can be used at up to 30wt% of some grease, may be costly, and have a supply chain in competition with other markets (e.g. electric vehicles).[16] Polymers are routinely used to increase the consistency of grease and reduce a portion of the need for thickener.

A comprehensive study was performed with low and high MW variants of six grease polymers, two tackifiers, and a dispersant PMA.

In all, 54 greases (6 base grease times 9 polymers) were prepared to screen for the influence of different greases and polymers in combination on the resulting NLGI grade. Samples where polymer improved the NLGI grade by $\geq$ 0.5 were later used in the roll stability study in the second half of this work.

Table 2 summarizes the observed changes in NLGI grade with the addition of polymers versus simply adding the diluent oil without polymer (the control). Out of 54 samples, 21 (39%) experienced no change in NLGI grade after adding 5wt% liquid grease polymer versus the control of 5wt% pure 100N diluent oil. 28 (52%) observed a half (39%) or full (13%) increase in NLGI grade. 5 samples (9%) lost NLGI grade by a half (7%) or full (2%) grade. "Half" grades are denoted as consistencies that fall within the gap of cone penetrations between two grades (e.g. an NLGI #1.5 falls between the NLGI #1 and #2 ranges).

Grease Category:	**Fibrous**		**Globular**		**Particulate**	
	Simple Lithium	**Lithium Complex**	**Calcium Sulfonate**	**Aluminum Complex**	**Silica**	**Bentonite Clay**
Control	1.5	2	2.5	2.5	**1**	**0**
Temp. Sens. Polymer (Low MW)	**2**	**3**		**2**	**2**	
Temp. Sens. Polymer (High MW)	**2**	**2.5**				
H-Bonding Polymer (Low MW)		**2.5**		**1.5**		**0.5**
H-Bonding Polymer (High MW)	**2.5**	**2.5**	**3**	**3**	**2**	**1**
Reactive Polymer (Low MW)	**2**	**3**	**3**			**0.5**
Reactive Polymer (High MW)	**2**		**2**	**3**		**0.5**
Tackifier (Low MW)	**2**	**2.5**	**3**	**2**	**2**	
Tackifier (High MW)	**2**		**3**			**0.5**
Dispersant PMA (High MW)	**2**		**2**			

Analytics:
of +0.0 NLGI:
21 (39%)
of +0.5 NLGI:
21 (39%)
of +1.0 NLGI:
7 (13%)
of -0.5 NLGI:
4 (7%)
of -1.0 NLGI:
1 (2%)

Table 2: NLGI grade of the 54 modified greases (with 5wt% of 8-10% polymer in oil) vs. controls (with 5wt% 100N). Blank entries mean no change (+0.0) to NLGI grade. **Bold** entries indicate a gain (+0.5 or +1.0). Red, a loss (-0.5 to -1.0).

Fibrous grease like simple lithium and lithium complex show high compatibility with the various grease polymers. 14 out of 18 (78%) grease/polymer combinations produced an increase in NLGI grade which indicates the interpenetrating network formation was successful. Higher consistency gains appear to occur with lower molecular weight variants of each grease polymer type. Two large (+1.0) grade changes occurred between lithium complex and low MW temperature sensitive and reactive polymers.

Globular grease like calcium sulfonate and aluminum complex were highly variable in response to grease polymer. Nearly half (39%) of prepared samples showed no effect on NLGI grade. One third produced a +0.5 increase and the remainder (28%) gave consistency losses with one -1.0 grade. Both globular greases favored higher MW additives: low and high MW tackifiers produced the best NLGI grade improvement in calcium sulfonate; aluminum complex gave NLGI grade improvement for high MW versions but lost grade with low MW versions of the same polymer type.

Negative changes to NLGI grade were not anticipated at the beginning of this study. Coincidentally globular structure greases, especially aluminum, that exhibited the NLGI grade loss have long been known to form “false body”.[17][18] Over time a grease during production and storage can increase in consistency over time as it ages. When the grease is sheared this extra consistency (false body) is quickly lost. On negative results for calcium and aluminum greases, false body may have caused the control to be higher NLGI grade but the addition of polymer inhibited false body leading to a lower grade with polymer. The net result would be a negative change in NLGI grade with polymer.

Particulate grease, silica and bentonite clay, produced either no change in NLGI grade with polymer or a mix of low and high NLGI grade increase. Modified silica grease results were dramatic with either a full NLGI grade improvement or no effect. The three cases where silica grease was improved occurred with additives that were subjectively adhesive in handling quality and OCP-based. Bentonite clay exhibited high compatibility and consistency gains primarily with polymers containing polar functionality, both hydrogen bonding and the polar-grafted reactive types. This result was reasonable due to the high surface functionality of –OH on clay which requires the use of hydrogen bonding dispersants to incorporate the clay into oil. Silicas, in contrast, tend to have lower surface functionality and less hydrogen bonding ability if produced from $SiCl_4$ at very high temperature as fumed silica rather than precipitated silica. This may explain the large difference in response to polymer between the two particulate greases.

3.2 Changes in Roll Stability with Polymer

Grease and polymer combinations that produced a notable increase in consistency ($\geq$ +0.5 NLGI grade) were considered to possess a strong interaction between the grease and polymer indicative of a stable interpenetrating network (IPN). Stable IPN formation has long been hypothesized to be the driving mechanism for most benefits to polymer in grease.

ASTM D1831 roll stability was used to evaluate the relationship between greases with strong IPN formation (showing high consistency increase) versus their shear stability. D1831 with ¼-cone measurements has a 11 point reproducibility; this gives a relative error of ±3.8% based on an average 290 cone penetration.

Twenty-seven polymer-modified grease samples were tested and compared against the roll stability changes of the control greases. **Table 3** summarizes the changes to consistency after ASTM D1831 roll stability with positive values meaning a loss of consistency (thinning) and negative values meaning an increasing in consistency (thickening). Samples within the 3.8% relative error of ASTM D1831 were deemed negligibly different.

Grease Category:	**Fibrous**		**Globular**		**Particulate**	
	Simple Lithium	**Lithium Complex**	**Calcium Sulfonate**	**Aluminum Complex**	**Silica**	**Bentonite Clay**
Control	+1.2%	+36.1%	+3.1%	+1.5%	+2.3%	+11.3%
Temp. Sens. Polymer (Low MW)		**+21.5%**			*+2.6%*	
Temp. Sens. Polymer (High MW)	*+1.5%*	**+19.8%**				
H-Bonding Polymer (Low MW)		*+37.9%*				*+11.5%*
H-Bonding Polymer (High MW)	*+1.5%*	**+25.6%**	+11.7%	+18.9%	+7.9%	*+9.4%*
Reactive Polymer (Low MW)	*-2.6%*	**+22.5%**	+9.8%	**-5.2%**		
Reactive Polymer (High MW)	*+0.0%*			+14.5%		*+12.5%*
Tackifier (Low MW)		**+17.8%**	*+4.6%*		*+2.6%*	
Tackifier (High MW)	*-2.1%*		*+1.6%*			*+13.8%*
Dispersant PMA (High MW)	+6.6%					*+8.6%*

Analytics:
 # Same
15 (56%)
 # More Stable
6 (22%)
 # Less Stable
6 (22%)

Table 3: ASTM D1831 roll stability changes in polymer modified greases. Blank entries were not tested. *Italic entries* indicate no significant change versus control (±3.8). **Bold** entries indicate improved roll stability (lower % change). Red entries indicate worse roll stability (higher % change).

Of the 27 samples, 15 samples (56%) demonstrated negligible changes, within error, to roll stability versus the control. The implication, however, is quite significant. Simple lithium and clay greases were improved by up to a full NLGI grade using polymer without an effect on shear stability. By reducing thickener to account for the polymers' effects, 0.45wt% polymer could replace up to 3.5wt% lithium 12-hydroxystearate preformed thickener or bentonite clay.[19][20]

6 samples (22%) showed an improvement in shear stability, the majority being lithium complex. **Figure 7** shows the highly structured nature of fibrous grease which can be destroyed during mechanical shearing. Lithium complex grease demonstrated high compatibility with most of the polymers tested showing both high NLGI grade improvement and reduced shear losses. These fibers are help together through weak, short-range ionic and hydrogen bonds and waxy interactions. Polymers diffused throughout this network provide strong covalent bonds over long-range to provide strength.

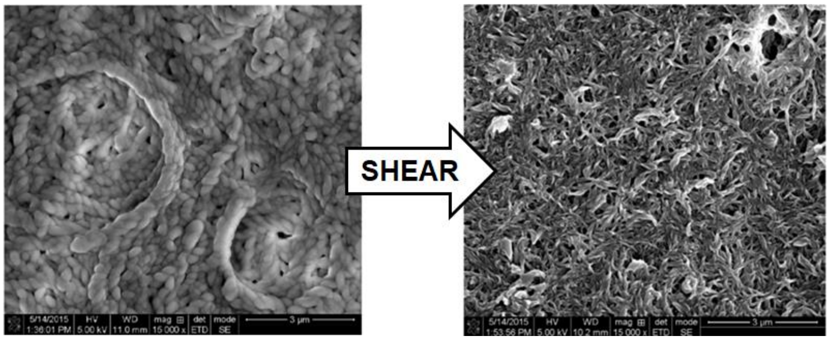


Figure 7: Damage to a fibrous grease structure; image from [21]

6 samples (22%) showed a loss of shear stability with the use of polymer. Four of six polymers that caused worse shear stability were high molecular weight hydrogen bonding polymers including the dispersant PMA. The majority of cases occurred with globular greases which tended to be highly 'selective' toward polymer – only a few polymers improved NLGI grade and qualified for roll stability testing. These globular greases tend to be held together by waxy interactions of long chain alkyl groups along the exterior of the micelles. It may be that large polymers with hydrogen bonding capability may be interrupting the structure of the micelles in order to hydrogen bond with the hydrophilic cores of

these structures. Reactive polymers also gave poor shear in the globular greases. These reactive additives operate by interacting with and grafting to the metal centers contained in the metal. This could inhibit the formation of stable micelles which make up the globular grease structure.

Oddly, three samples exhibited negative roll stabilities, i.e. showed higher consistency after shear than before shear.. Two of the samples occurred with the low molecular weight reactive grease polymer, a negligible result in simple lithium and a significant result (>3.8 difference) in aluminum complex. There may be many explanations or competing effects that leads a grease to become tougher after shearing. Since the common element was the reactive polymer it is hypothesized that the reactive polymer generated a weak but fast-forming kinetic product which rearranged to a more stable thermodynamic product with the aid of aggressive milling in the ASTM D1831 experiment.[22] For example, the reactive functionality, which can coordinate metals like a diacid or complex hydroxyls like boron, may have switched between one mode of action and the other.

3.3 Overall Comments on Findings

The stark contrast between the effects of polymer on NLGI grade and yield of lithium versus non-lithium grease demonstrate the need to include a variety of grease types in additive research. However, lithium continues to remain a majority (>70%) of the market and subsequently the focus of much R&D.[23] This work specifically includes six grease types to expand the body of work available on polymer/grease interactions. Lithium greases behaved as expected because most expectations for grease polymer performance are made using lithium grease. The results in globular and particulate greases were far more nuanced.

Prior to this study there was much data to support that polymers are generally good for improving shear stability. However, the results above show that only 22% of 27 cases tested resulted in significant improvement and the remaining 78% showed either a loss of stability or no change. Yet only 22% of the cases showed a defined loss of shear stability (increasing roll stability changes) from adding polymer. This signifies that the majority of times polymer is used for water resistance, tack, adhesion, oil bleed control, or added yield will not come at the expense of mechanical stability. These losses occurred primarily for a specific group of grease polymers (hydrogen bonding type) in a specific category of grease (globular structure like Ca and Al) which may now be better anticipated at the beginning of a formulation project due to these findings.

With regards to yield, many cases (52%) demonstrated that grease polymers can increase NLGI grade which ultimately means improved yields and economics after replacing more thickener with oil. A small number of cases showed NLGI grade loss which may be from reducing occurrence of false body. Cases of no NLGI grade change may actually be an opportunity to add that polymer for a different advantage without having to reformulate the thickener and oil content.

4. Conclusions

Do polymers affect the mechanical stability of grease? The results with ASTM D1831 roll stability show that polymers are primarily neutral with changes on the order of the precision of D1831 can increase or decrease NLGI grade for a base grease but.

The results of this study are intended as a starting point for formulators and not a definitive guide. Most greases, even of the same kind, will vary widely by factors like the specific thickener used, the base oil, NLGI grade, and production.

Grease is a highly complex material where simple changes to composition or process can have complicated results on performance.

Tools like the interpenetrating network concept provide high level strategies for narrowing right polymer for a grease but much empirical work in optimization remains. Thus grease remains both an art and a science.

This study elaborates on the interpenetrating network model of grease/polymer interactions and importantly considers a wide variety of grease types. It is shown here that not all grease polymers form IPN in all greases and the best option will vary for each grease. Even when an IPN did form (suggested by increases in NLGI grade) not all the proposed benefits of an IPN were obtained (lack of shear stability improvement).

Acknowledgements

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