Grease Polymers and Their Benefits to Grease

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Overview

- **Grease Polymers**
  - What are they?
  - Three types

- **G.R.E.A.S.E.**
  - Benefits
  - Performance data
  - Test methods

Polymers in Grease

- **“Grease polymer”**
  - Provide tack, mechanical strength, water resistance, NLGI grade
  - Helps grease to perform well: lubricate, seal, stay in place
  - Different than polymers for lube oil: engine, HF, gear

Networks Working Together

Grease is like concrete

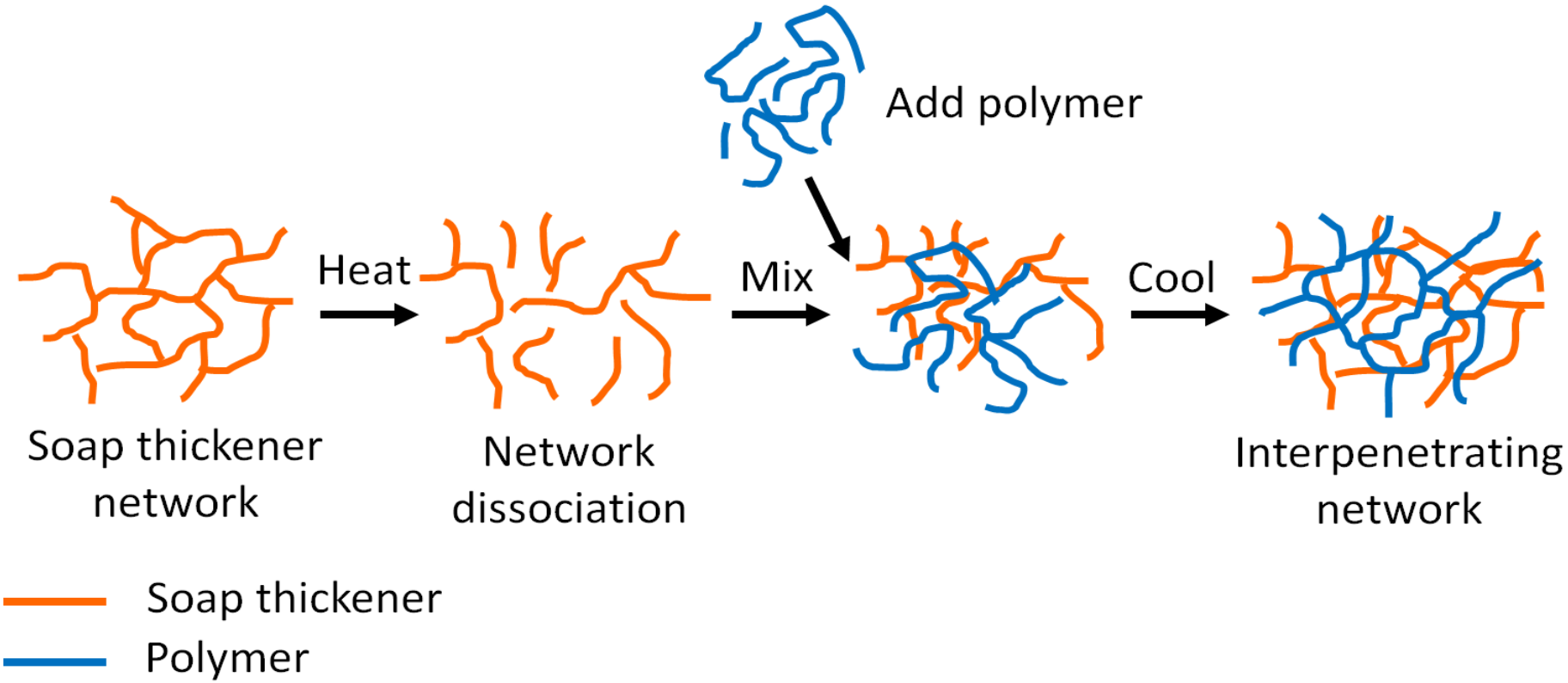
- Tough but brittle
- Short-range structure
- Small molecules (<500 g/mol)

Polymer is like rebar

- Flexible
- Long-range structure
- Large molecule (100k – 1M)

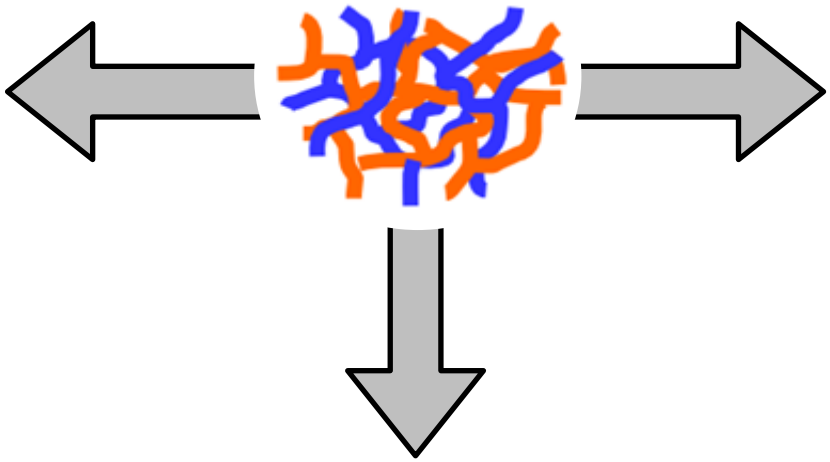
Interpenetrating Network

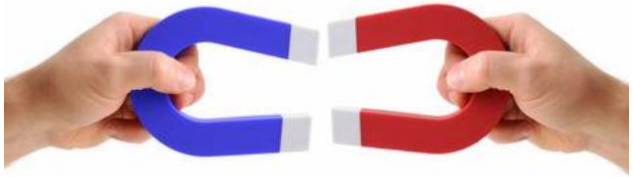
- Abbreviated “IPN”



- Polymer needs special functionality to form the IPN

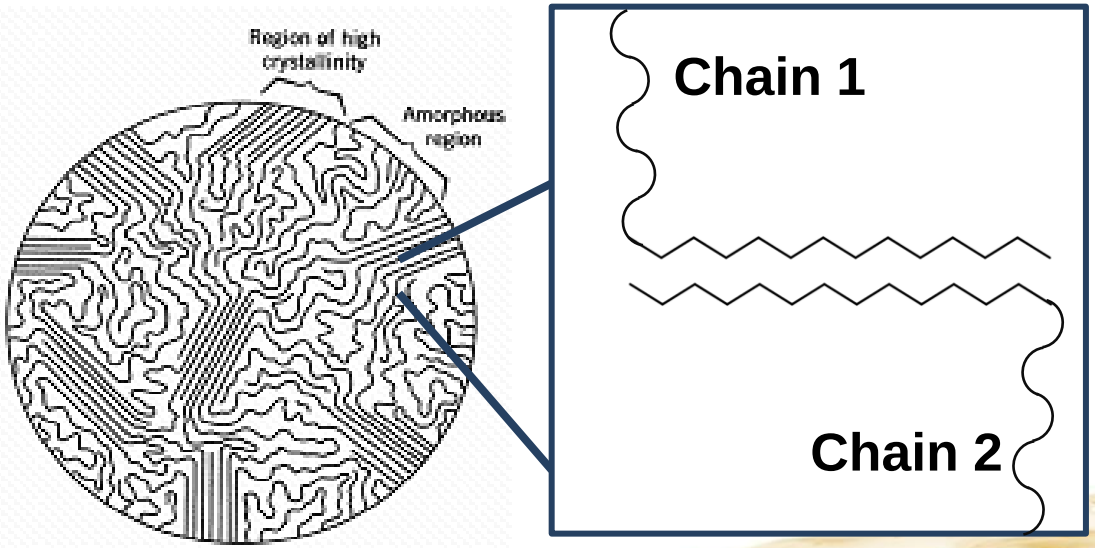
Three Types of Grease Polymers





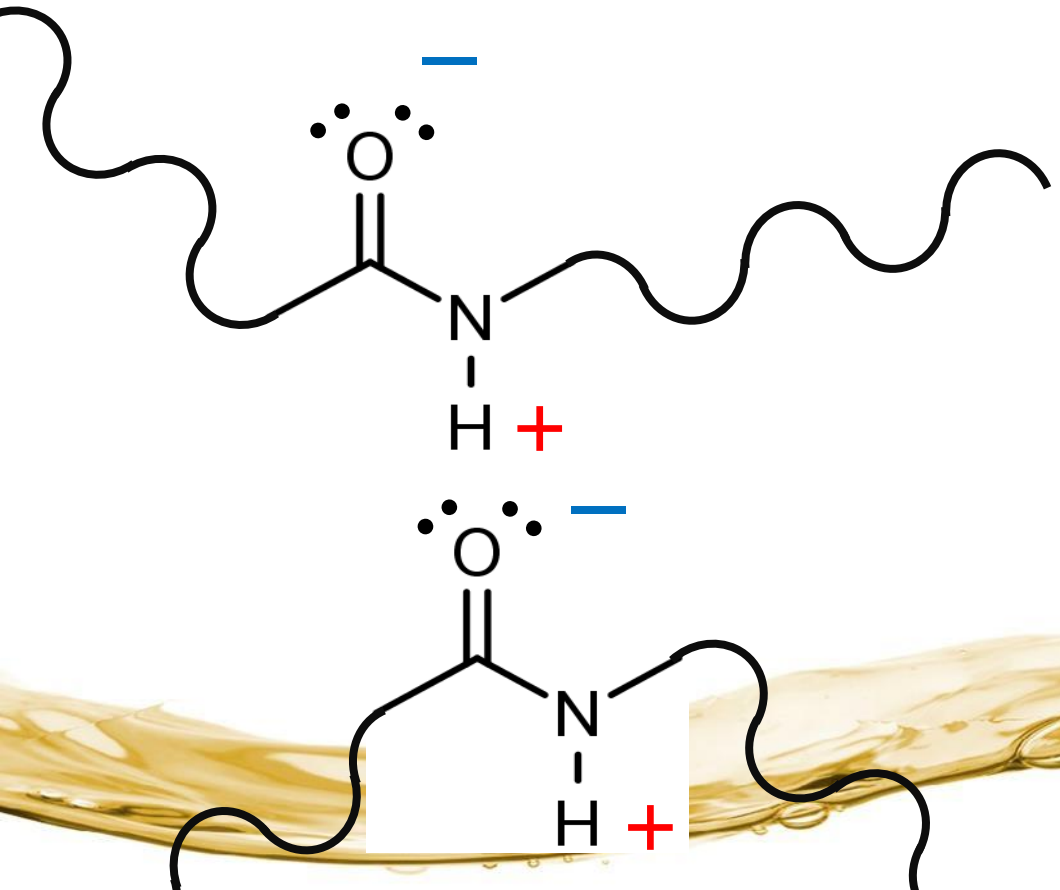
1. Temperature Sensitive

- Olefin copolymers (OCP)
  - High ethylene or styrene content – “semi-crystalline”
  - Associate like Velcro (hook-and-loop) tape after cooling



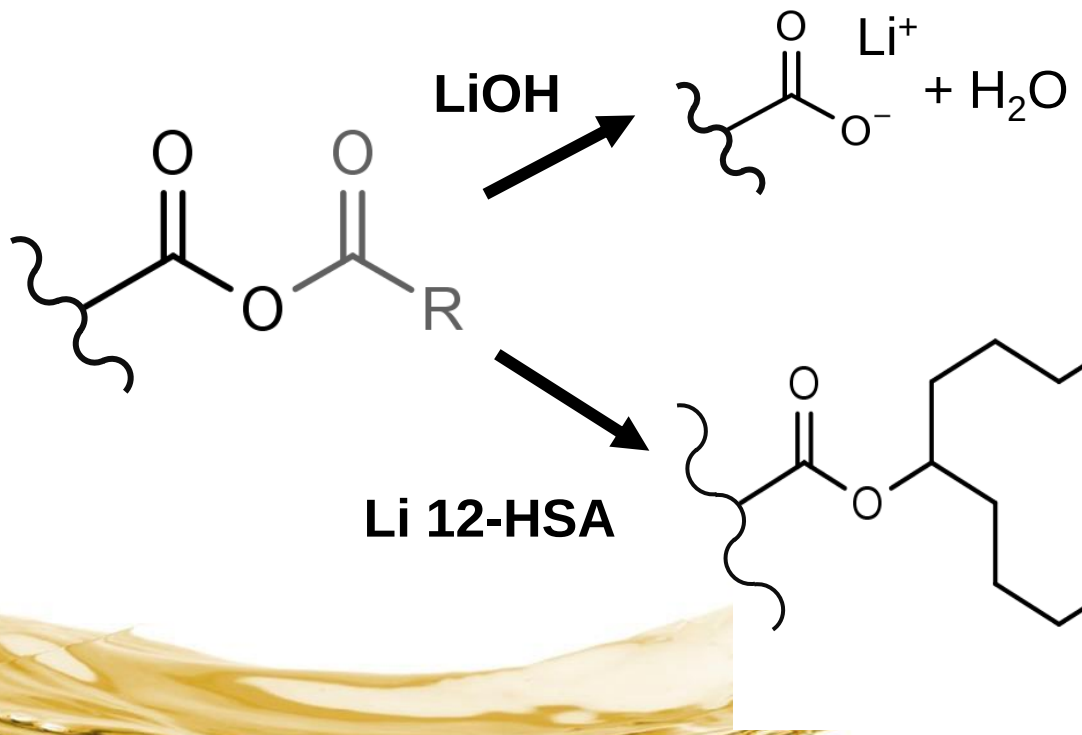
2. Hydrogen Bonding

- Poly- esters, amides, ureas, alcohols, amines, etc.
  - Positive hydrogens attract negative oxygen and nitrogen
  - Most useful in biobased greases, or silica and clay grease



3. Reactive

- Polymers grafted with reactive anhydride species
  - Coordinate with Li^+, Ca^{2+}, etc. like a diacid
  - Complex with –OH on 12-HSA like a boron ester



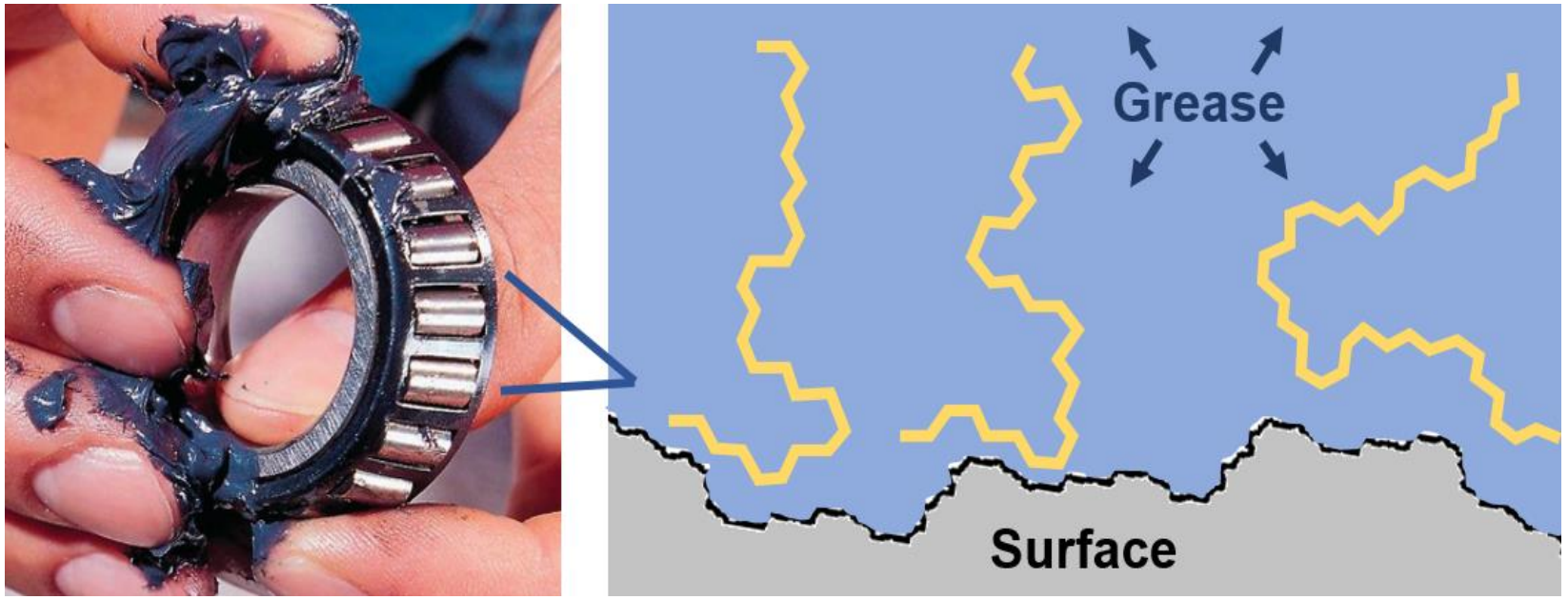
Benefits

Greater Adhesion
Reduced Bleeding
Elevated Tackiness
Added Yield
Superior Shear Resistance
Enhanced Water Resistance

Greater Adhesion

- **“Adhesive tack”**
  - Reinforcement of attachment between the grease and a surface

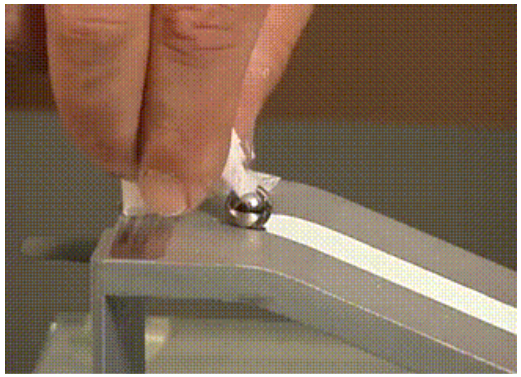
- Lower MW polymers which diffuse into asperities, act as anchors



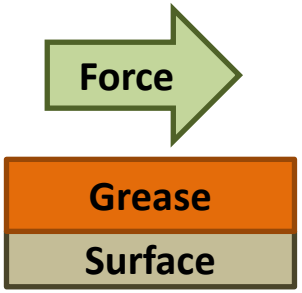
- Test methods: many tests for adhesion but no standard for grease adhesion

Adhesion Test Methods

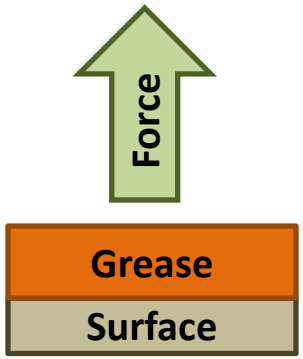
D3121 – Rolling ball tack test



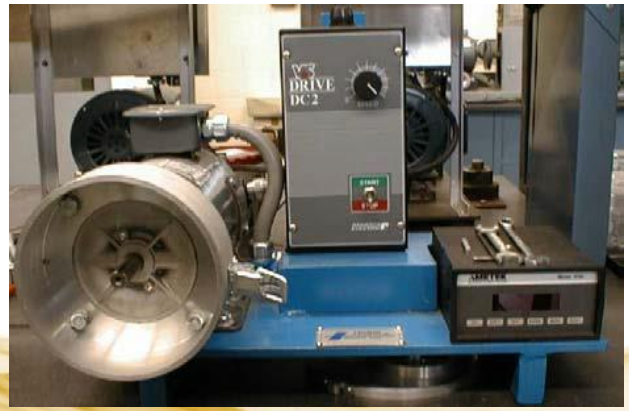
Animated: ChemInstruments, 2015

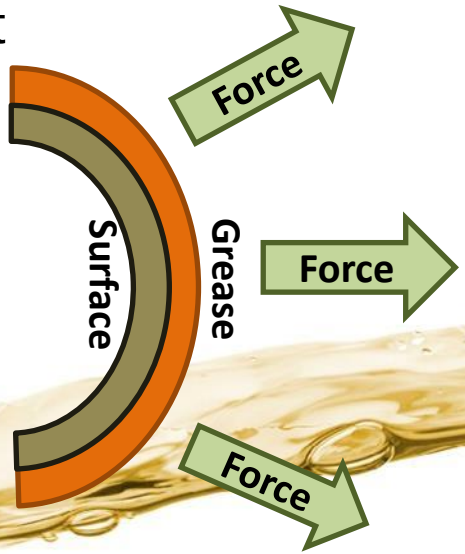


Pull-Off Force Test (2014, FPI)



Mobil Grease Fling-Off Test



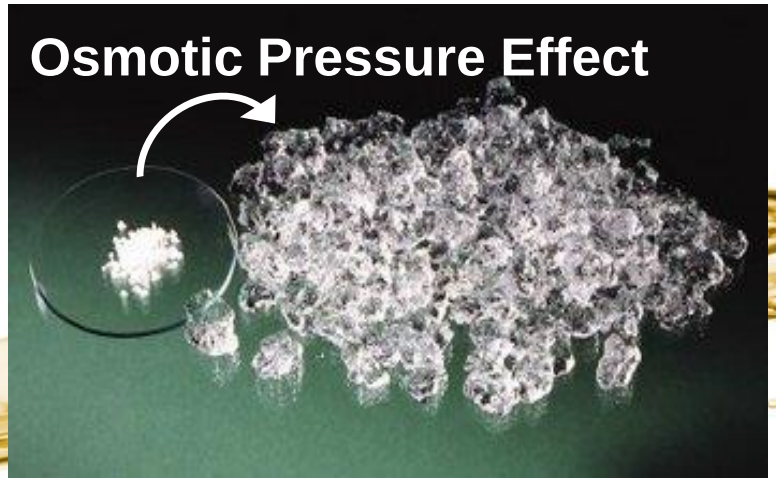


Reduced Bleeding

- Oil is about 70-90% of grease
- Non-polar oil rejects polar thickener
- Bleed causes NLGI grade change and customer complaints

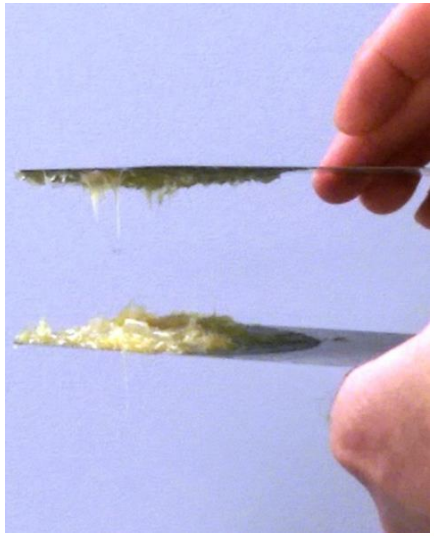
Oil Bleed Performance

	D6184 Oil Bleed
NLGI #2 Calcium Sulfonate base grease	**3.30**
1% liquid OCP tackifier	-24.6%
2% liquid OCP tackifier	-32.0%
1% solid styrene OCP	-35.3%
1% solid semi-crystalline OCP flake	-49.3%
3% liquid reactive polymer	-52.2%
1% solid 50 SSI OCP	-74.9%
1% solid crystalline OCP	-80.3%
1% liquid rubber emulsion	-86.0%

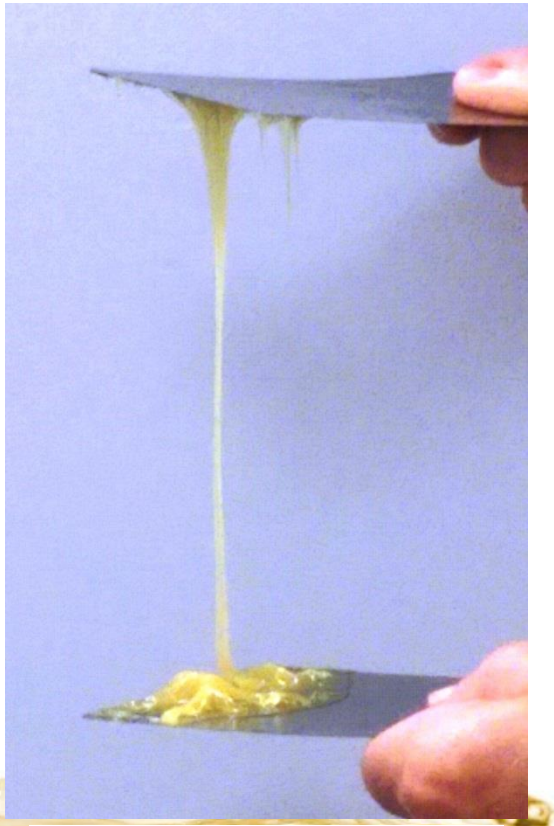


Elevated Tackiness

- **“Cohesive tack”**
  - Reinforcement of the internal structure of grease
  - Higher MW polymers more cohesive



No Polymer

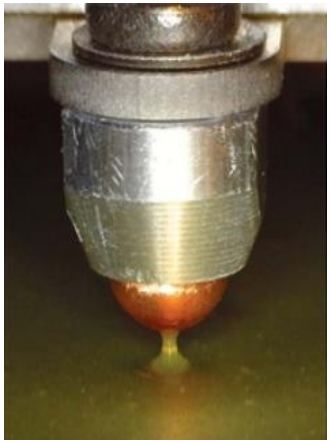


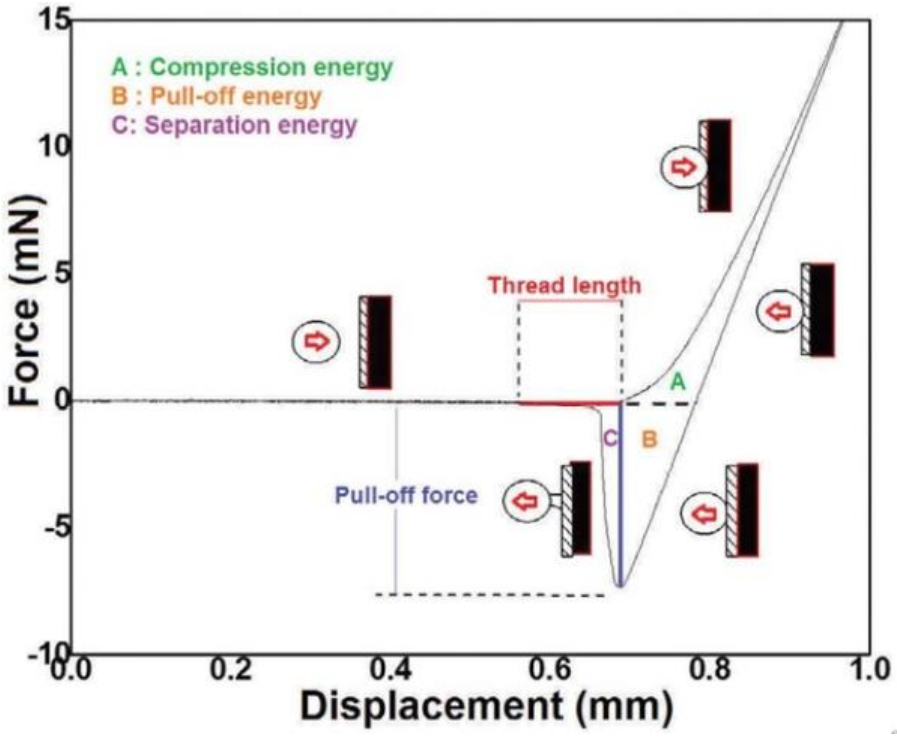
2% PIB Tackifier

Tackiness Testing

- Modified pull-off force with gauge (FPI, 2014)

- Tack adhesion tester (Falex and FPI, 2019)
  - Force gauge on cantilevered copper probe

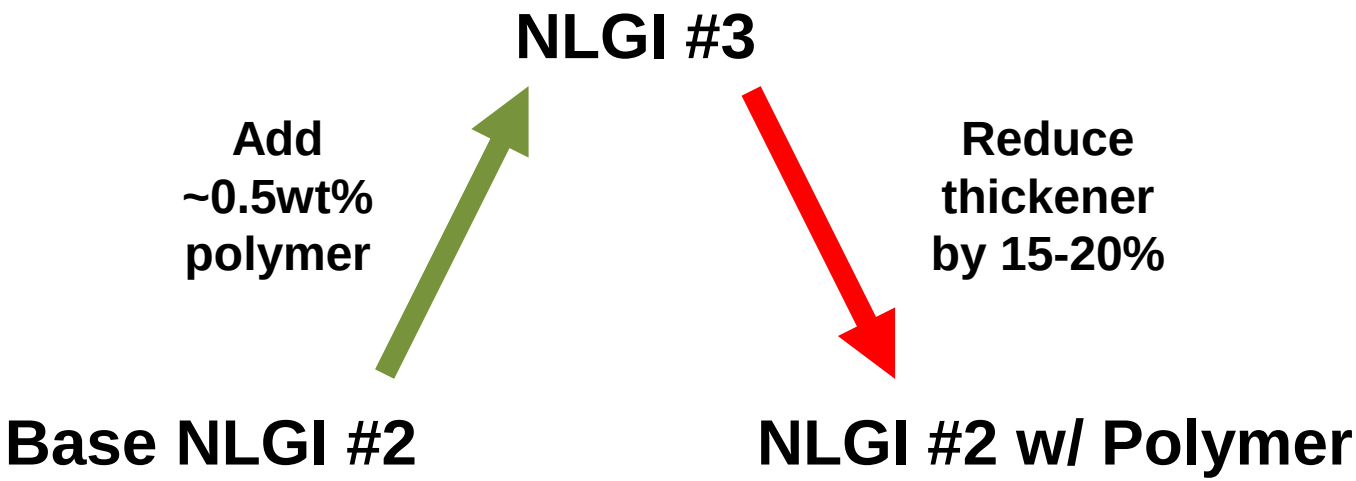




"Quantitative evaluation of tackiness...", D. Vargo, Lube Magazine, Feb. 2014
“On the Right Tack", M. Moon, Lubes n' Greases, Oct. 2018
“Measuring Grease Tackiness Objectively”, Falex and Functional Products, ELGI AGM 2019

Added Yield

- Polymers provide increased consistency
  - Less thickener needed to meet target NLGI grade
    - More kilograms of grease per kg of thickener



- Test method: D217 (cone penetration), D1403 (½-,¼-cone)

Grade Changes

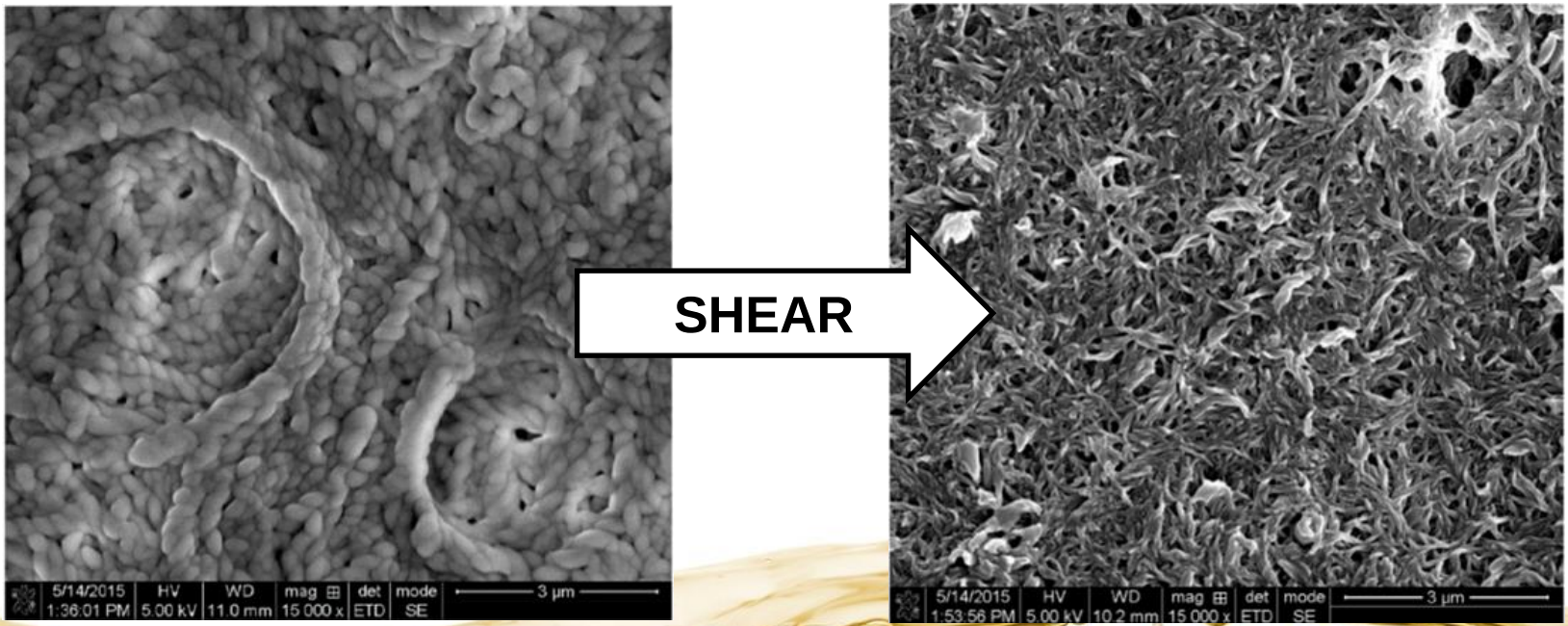
- NLGI grade change with 0.45wt% grease polymer added:
  - 52% = Increase in grade
  - 39% = No change
  - 9% = Decrease in grade

	Simple Lithium	Lithium Complex	Calcium Sulfonate	Aluminum Complex	Silica	Bentonite Clay
Control	1.5	2	2.5	2.5	1	0
Temp. Sens. Polymer #1	2	*3*		2	*2*	
Temp. Sens. Polymer #2	2	2.5				
H-Bonding Polymer #1		2.5		1.5		0.5
H-Bonding Polymer #2	*2.5*	2.5	3	*3*	*2*	*1*
Reactive Polymer #1	2	*3*	3			0.5
Reactive Polymer #2	2		2	*3*		0.5
Tackifier #1	2	2.5	3	2	2	
Tackifier #2	2		3			0.5
Dispersant PMA	2		2			

Willett, E. Do Polymers Affect the Mechanical Stability of Grease? (manuscript in prep). NLGI 87th Annu. Meet. (2020).

Superior Shear Resistance

- Shear originates from high loads and speeds
- Results in changes to NLGI grade and physical properties
- Higher “mechanical stability” resists shear



Rezasoltani, A. On Monitoring Physical and Chemical Degradation and Life Estimation Models for Lubricating Greases. Lubricants 2016, 4, 34.

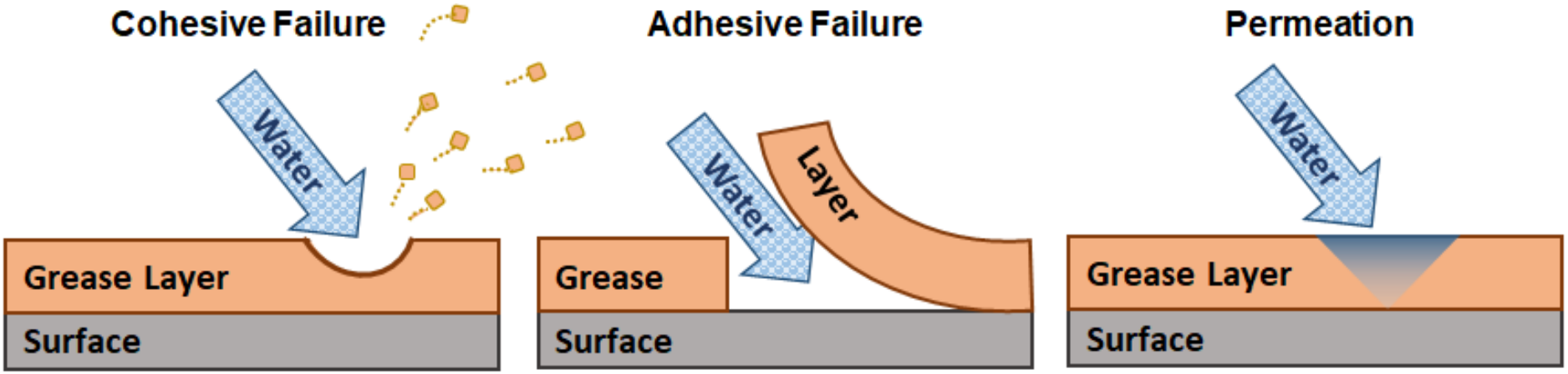
Shear Changes

	10K Stroke, D217 (% Change)	Roll Stability, D1831 (% Change)
NLGI #2 Lithium Complex (cone = 296)	+8.1%	+11%
+0.5% solid styrene OCP	+2.4%	--
+1% solid styrene OCP	+1.3%	+4.8%
+2% solid styrene OCP	+1.0%	--
+0.75% solid semi-crystalline OCP	+3.0%	
+1% solid semi-crystalline OCP	+1.7%	+4.4%
+2% liquid OCP tackifier	--	+4.1%
+3% liquid reactive polymer	--	+1.4%
+1% solid crystalline OCP	--	+0.5%

88% reduction

Enhanced Water Resistance

- Greatly improved water spray-off and wash-out resistance
  - Adhesive + cohesive tack resists physical removal of grease
  - Increased surface tension – less water absorbed into grease porosity



- Test methods: water spray-off (D4049), water washout (D1264)

WSO/WWO Performance

- Effectiveness depends on the match between polymer and grease

	WSO (D4049)	WWO (D1264)
NLGI #2 Lithium Complex	**52%**	**26%**
+1% solid semi-crystalline OCP	24%	11%
+1% solid styrene OCP	9%	12%
+1% liquid reactive polymer	23%	14%
+0.25% solid reactive polymer	26%	25%
+4% blend of OCP and reactive	7%	2%
NLGI #2 Calcium Sulfonate	**72%**	-
+0.5% solid semi-crystalline OCP	16%	-
+1% solid semi-crystalline OCP	7%	-
+0.25% solid reactive polymer	47%	-
+0.5% solid reactive polymer	4%	-
NLGI #2 Clay Grease	**49%**	0.0%
+5% liquid OCP	48%	1.3%
+4% liquid reactive polymer	12%	-2.2%
+1% liquid rubber emulsion	10%	29%

Summary

- Polymers are used to influence the performance of grease
- Three types of grease polymer form an interpenetrating network (IPN)
- Benefits include:
  Greater Adhesion
  Reduced Bleeding
  Elevated Tackiness
  Added Yield
  Superior Shear Resistance
  Enhanced Water Resistance