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A Study of Polymer Additives in Mineral and Vegetable Oil-based Greases

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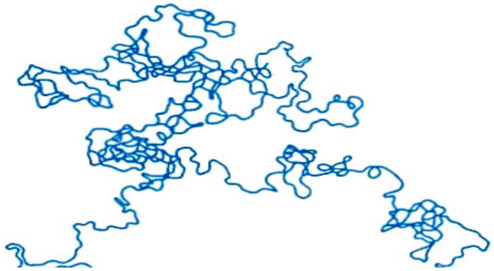
- **The benefit of considering polymers in grease.**
- **How polymers grease form networks in grease**
- **Why polymers are compatible with mineral or vegetable oil.**
- **Polymer structure**
- **Polymer compatibility with grease- ability to form an interpenetrating network**
- **Experiments of polymer in mineral and vegetable grease**
- **Summary**

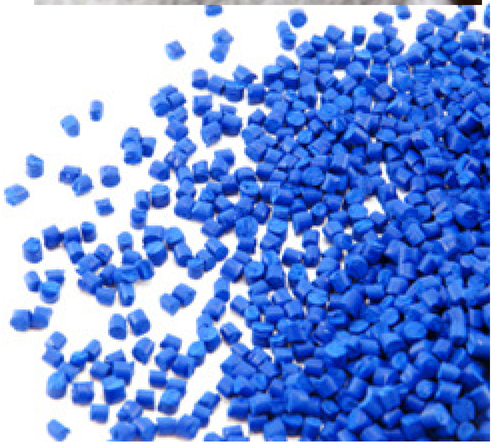
The benefits of polymer in grease

- **G**reater Adhesion
- **R**educed Bleeding
- **E**levated Tackiness
- **A**dded Yield
- **S**uperior Shear Resistance
- **E**nhanced Water Resistance

These improvements are associated with the long chain nature of polymer.



http://capolight.files.wordpress.com/



The structure of grease

Grease composition

- ❑Base fluid (liquid phase): 70-90%
- ❑Thickener (solid phase): 5-25%
- ❑Other additives

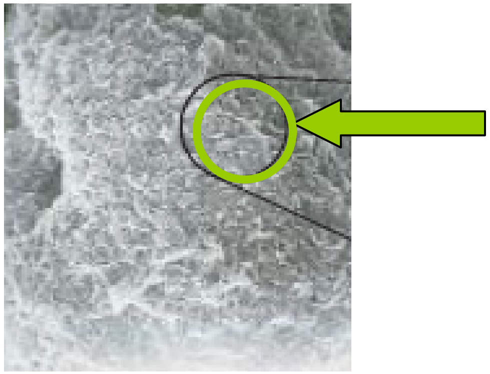
Thickener:

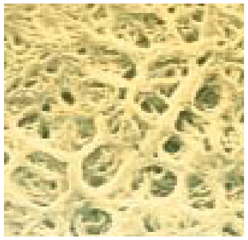
- ❑Soap thickeners
- ❑Non-soap thickeners:
  e.g. : Organic thickener (Polymer)
  Inorganic thickener (clay, silica gel, etc.)

Multi-phase structure of grease

❑The solid phase thickener provides a physical matrix to hold the liquid phase base fluid in a semi-solid structure until operating conditions.
❑The soap thickeners possess interlocked fibrous structure.

Multi-phase morphology of grease





Network matrix

Electron microscopy micrograph of soap particles in a sample of lubricating grease

"The chemistry and physics of grease" Axel Christiernsson White paper 2004/ 01

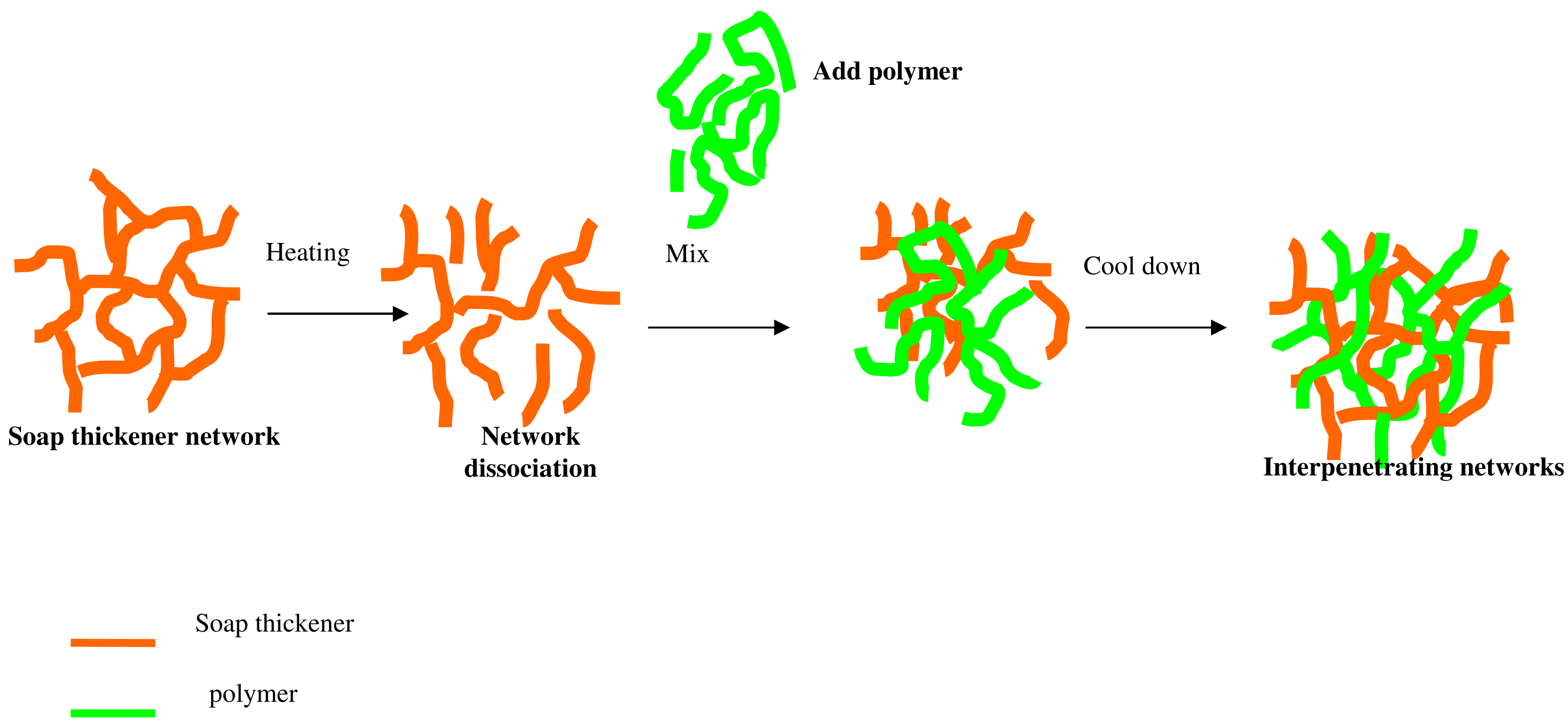
http://www-v3.physics.utoronto.ca/overview/history/microsco/microapp.htm

Mechanism

❑In order to enhance the structure and the mechanical properties of grease, the polymer has to form a three dimension network by itself or interact with the network formed by another thickener like soap thickener.

❑Both grease and polymer networks are flexible and reversible. The grease fiber network entangles with the polymer network and forms interpenetration networks (IPNs).

The scheme of the formation of IPNs



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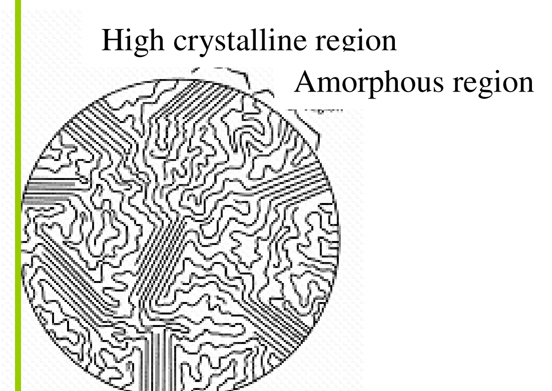
Polymer selection criteria

- ❑ **Compatible with base oil**
- ❑ **Ability to form physical networking structure in the grease**
  - ❑ **Semi-crystalline polymer (e.g. polyolefin copolymer with high ethylene loading)**
  - ❑ **Temperature sensitive solubility (e.g. polyolefin/styrene block copolymer)**
  - ❑ **Hydrogen bonding (e.g. polyurea or polyolefin with amide groups)**
  - ❑ **Long chain entanglement (e.g. super high molecular weight polyolefin)**

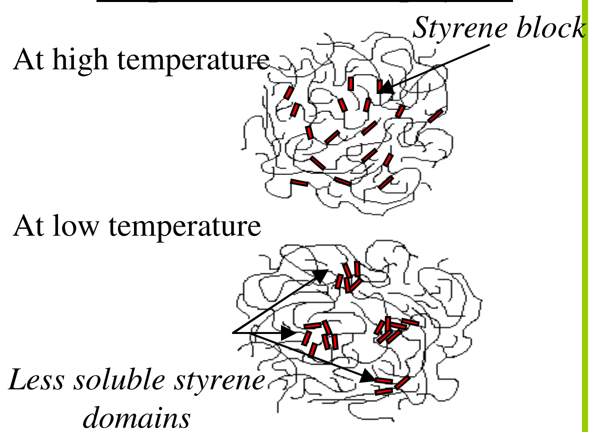
Scheme of network formed by crystalline structure of polymer



Semi-Crystalline polymer

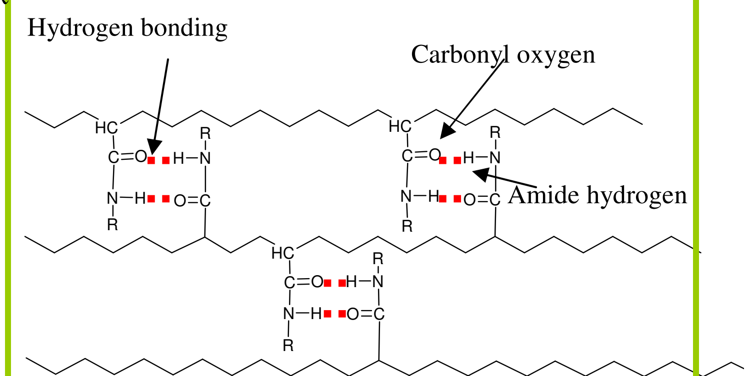
http://lww.kt.dtu.dk/~vigild/2005_06_hempel/Theory/Polymers%20in%20general.htm

Scheme of network formed by solubility temperature sensitive polymer



Polyolefin/styrene block copolymer

Scheme of network formed by hydrogen bonding



Hydrogen bonding in amide grafted polyolefin

Mineral oil

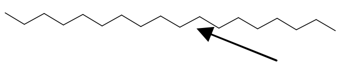
Base oils from difference resources:

- ❑Petroleum-derived (Mineral oil)
- ❑Synthetics (PAO, Synthetic ester, synthetic ether, silicones, etc.)
- ❑Plant or animal based (soybean, rapeseed/canola, castor, palm, sunflower, etc.)
- ❑Others

Chemistry of Mineral oil :

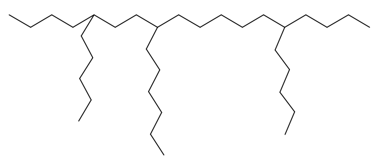
- ❑Paraffinic oils (based on alkanes)
- ❑Naphthenic oils (based on Cycloalkanes)
- ❑Aromatics oils

Examples:

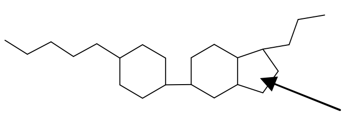


Saturated linear chain

(a) linear alkane

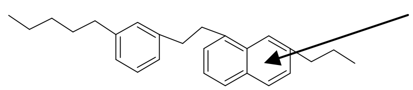


(b) branched alkane



Cyclic ring

(c) Cycloalkanes with alkane chain



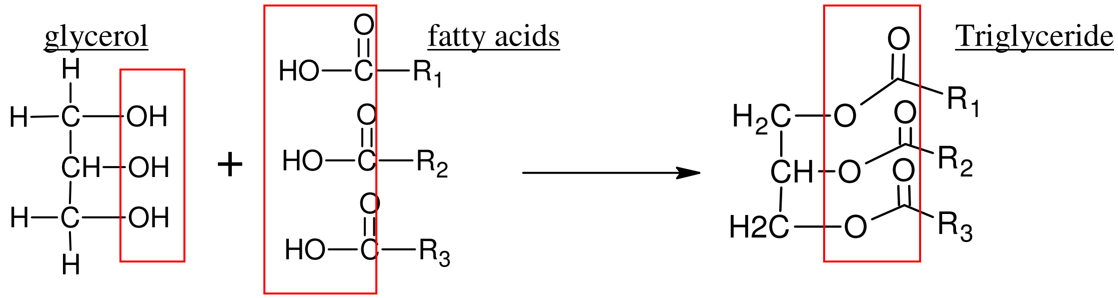
aromatic ring

(d) aromatics with alkane chain

Vegetable oil

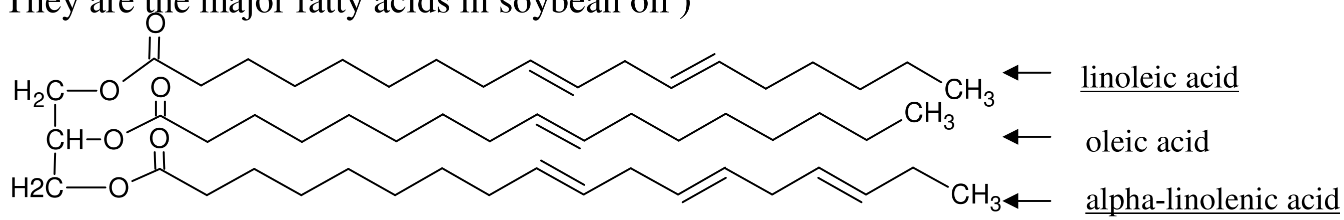
Chemistry of vegetable oil :

The major component in vegetable oil is triglyceride.
(An ester derived from glycerol and fatty acids.)



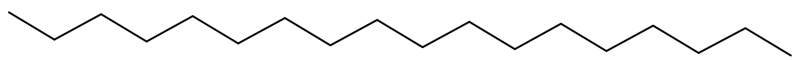
Triglyceride is formed from glycerol and fatty acids (R1, R2 and R3 represent different unsaturated and saturated hydrocarbon chains)

Example of a triglyceride:
an unsaturated fat triglyceride from etherification of glycerol with linoleic acid, oleic acid and alpha-linolenic acid.
(They are the major fatty acids in soybean oil)



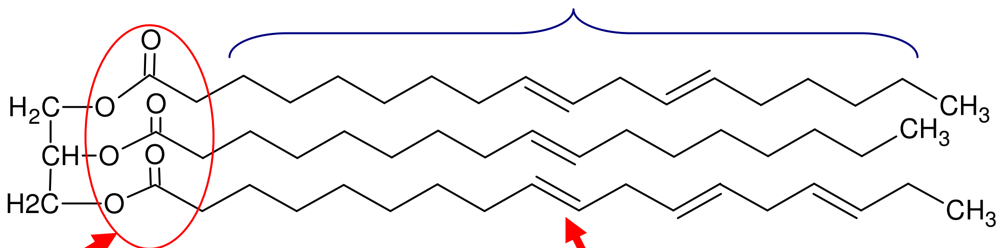
Structure differences between vegetable oil and paraffinic oil

- **Linear paraffinic oil:**



Similarity: Long hydrocarbon chain

- **Triglyceride:**



Difference: Polar Ester groups

Difference: Unsaturated double bond

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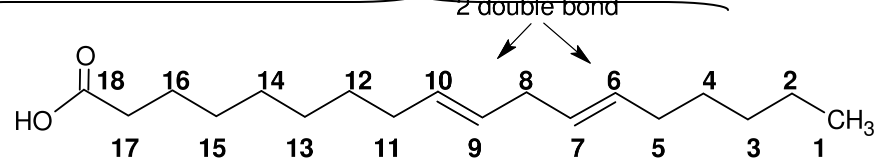
Fatty acids in different refined vegetable oils :

No double bond / one double bond / multi double bond

Fatty Acids		Almond	Apricot kernel	Avocado	Canola	Coconut	Corn	Cottonseed	Flaxseed	Grapeseed	Hazelnut
Common Name	Saturated										
Caproic acid	6:0					0.6					
Caprylic acid	8:0					7.5					
Capric acid	10:0					6.0					
Lauric acid	12:0					44.6					
Myristic acid	14:0					16.8	0.24	0.8		0.1	0.1
Palmitic acid	16:0	6.5	5.8	10.9	4.0	8.2	10.58	22.7	5.3	6.7	5.2
Margaric acid	17:0						0.07				
Stearic acid	18:0	1.7	0.5	0.66	1.8	2.8	1.85	2.3	4.1	2.7	2.0
Arachidic acid	20:0				0.7		0.43				
Behenic acid	22:0				0.4						
Lignoceric acid	24:0				0.2						
Total		**8.2**	**6.3**	**11.56**	**7.1**	**86.5**	**13.17**	**25.8**	**9.4**	**9.5**	**7.3**
	Monounsaturated										
Palmitoleic acid	16:1	0.6	1.5	2.67	0.2		0.14	0.8		0.3	0.2
	17:1										
Oleic acid	18:1	69.4	58.5	67.89	56.1	5.8	27.33	17.0	20.2	15.8	77.8
Gadoleic acid	20:1				1.7						
Erucic acid	22:1				0.6						
Total		**70**	**60**	**70.56**	**58.6**	**5.8**	**27.47**	**17.8**	**20.2**	**16.1**	**78**
	Polyunsaturated										
	Omega 6										
Linoleic acid	18:2n6	17.4	29.3	12.53	20.3	1.80	53.52	51.5	12.7	69.6	10.1
Arachidonic acid	20:4n6							0.1			
	Total n6	17.4	29.3	12.53	20.3	1.80	53.52	51.6	12.7	69.6	10.1
	Omega 3										
Alpha linolenic acid (ALA)	18:3n3	0	0	0.96	9.3	0	1.16	0.20	53.3	0.1	0
	Total n3	0	0	0.96	9.3	0	1.16	0.20	53.3	0.1	0
Total Poly		**17.4**	**29.3**	**13.49**	**29.6**	**1.80**	**54.68**	**51.8**	**66**	**69.7**	**10.1**
	Ratio n6/n3	no n3	no n3	13.1	2.2	no n3	46.1	258.0	0.24	696.0	no n3

Units: grams fatty acids per 100 grams oil

Example: linoleic acid   18 carbon atoms on the fatty acid chain



http://www.thepaleodiet.com/nutritional_tools/oils_table.html

Fatty acids in different refined vegetable oils :

Fatty Acids		Mustard	Oat	Olive	Palm	Peanut	Rice bran	Safflower	Sesame	Soybean	Sunflower	Walnut	Wheat germ
Common Name	Saturated												
Caproic acid	6:0												
Caprylic acid	8:0												
Capric acid	10:0												
Lauric acid	12:0		0.39		0.1								
Myristic acid	14:0	1.39	0.24		1.0	0.1	0.7			0.1			0.1
Palmitic acid	16:0	3.75	16.67	10.93	43.5	9.5	16.9	4.29	8.9	10.3	5.9	7.0	16.6
Margaric acid	17:0												
Stearic acid	18:0	1.12	1.05	1.98	4.3	2.2	1.6	1.92	4.8	3.8	4.5	2.0	0.5
Arachidic acid	20:0			0.42		1.4							
Behenic acid	22:0			0.13		2.8							
Lignoceric acid	24:0					0.9							
Total		**6.26**	**18.35**	**13.46**	**48.9**	**16.9**	**19.2**	**6.21**	**13.7**	**14.2**	**10.4**	**9**	**17.2**
	Monounsaturated												
Palmitoleic acid	16:1	0.22	0.2	1.16	0.3	0.1	0.2		0.2	0.2		0.1	0.5
111	17:1			0.14									
Oleic acid	18:1	11.61	34.9	72.29	36.6	44.8	39.1	14.36	39.3	22.8	19.5	22.2	14.6
Gadoleic acid	20:1	6.19		0.31	0.1	1.3			0.2	0.2		0.4	
Erucic acid	22:1	41.18											
Total		**59.2**	**35.1**	**73.9**	**37**	**46.2**	**39.3**	**14.36**	**39.7**	**23.2**	**19.5**	**22.7**	**15.1**
	Polyunsaturated												
	Omega 6												
Linoleic acid	18:2n6	15.33	39.08	9.21	9.1	32	33.4	74.6	41.3	51.0	65.7	52.9	54.8
Arachidonic acid	20:4n6												
	Total n6	15.33	39.08	9.21	9.1	32	33.4	74.6	41.3	51	65.7	52.9	54.8
	Omega 3												
Alpha linolenic acid (ALA)	18:3n3	5.90	1.79	0.79	0.2	0	1.6	0	0.3	6.8	0	10.4	6.9
	Total n3	5.9	1.79	0.79	0.2	0	1.6	0	0.3	6.8	0	10.4	6.9
Total Poly		**21.23**	**40.87**	**10**	**9.3**	**32**	**35**	**74.6**	**41.6**	**57.8**	**65.7**	**63.3**	**61.7**
	Ratio n6/n3	**2.6**	**21.8**	**11.7**	**45.5**	**no n3**	**20.9**	**no n3**	**137.7**	**7.5**	**no n3**	**5.1**	**7.9**

Units: grams fatty acids per 100 grams oil

http://www.thepaleodiet.com/nutritional_tools/oils_table.html

Polymer structure

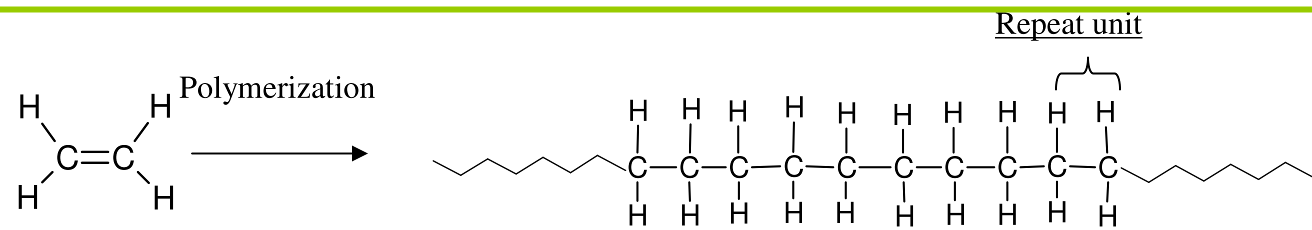
What is polymer?

❑Polymer is a high molecular weight molecular composed of repeating structure units and the repeating units are connected by covalent chemical bonds. It is typically formed from polymerization of monomers.

❑The chemical structure of repeating unit, the number of the repeating unit in the polymer chain, the patterns the repeating unit connected to each other and other factors determine the property of a particular polymer.

What is polyolefin?

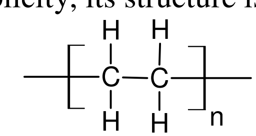
❑Polyolefin is a group of polymers from the polymerization of alkene monomers (alkenes have chemical formula as C_nH_{2n}). (e.g. polyethylene, polybutadine, polysiobutylene)



Ethylene monomer

Polyethylene polymer

For simplicity, its structure is expressed as:

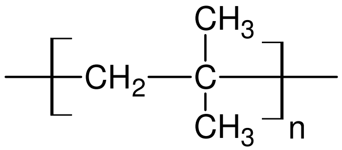


n is the repeating number

Polymers used in this study

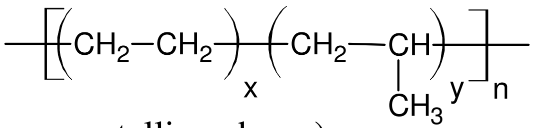
Polyolefin:

Polyisobutylene (PIB)



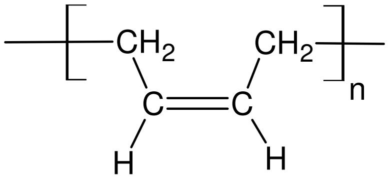
(Saturated hydrocarbon)

Ethylene/propylene copolymer (OCP)



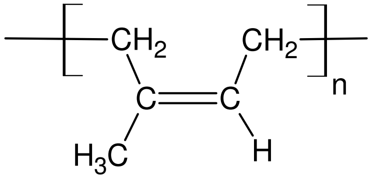
(Saturated hydrocarbon; High ethylene loading in OCP can form crystalline phase)

Polybutadiene (PB)



(unsaturated hydrocarbon)

Polyisoprene (PIP)

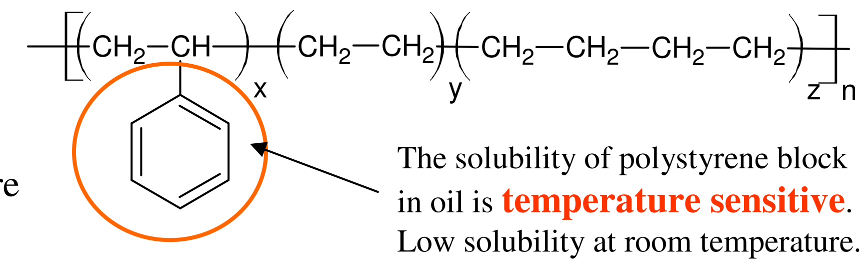


(unsaturated hydrocarbon)

Polymers used in this study

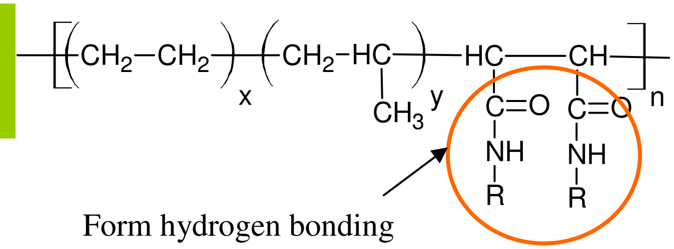
Polyolefin: Modified with Functional Groups

Styrene-ethylene-butylene copolymer (SEBCP)



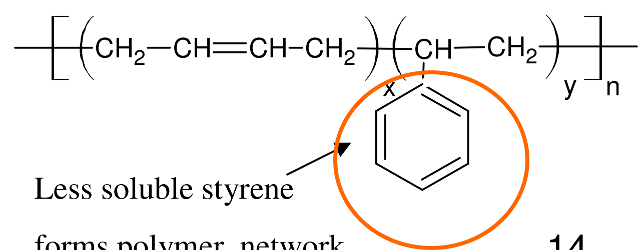
(saturated hydrocarbon with rigid and solubility temperature sensitive styrene)

Ethylene/propylene copolymer grafted with amide (OCP-A)



(saturated hydrocarbon with polar amide group on the side chain)

Styrene-butadiene copolymer (SBR)

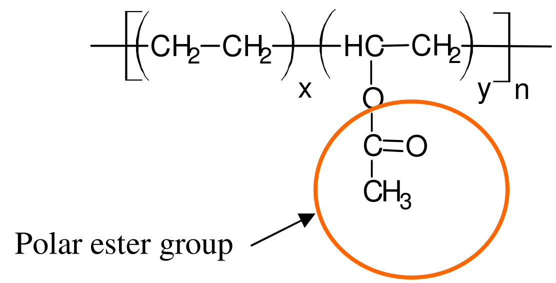


(unsaturated hydrocarbon with rigid and less soluble styrene)

Polymers used in this study

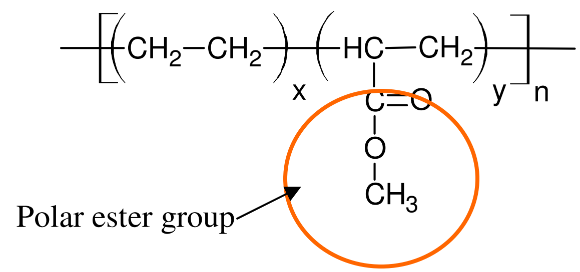
Ethylene/vinyl acetate copolymer (EVA)

(saturated hydrocarbon with polar ester group of vinyl acetate)



Ethylene/methylacrylate copolymer (EA)

(saturated hydrocarbon with polar ester group of methylacryate)



The solubility of polymer in base oil

Polymer	Paraffinic oil (Mineral oil)	Soybean oil (vegetable oil)
Ethylene/propylene copolymer (OCP)	soluble	insoluble
polyisobutylene (PIB)	soluble	insoluble
OCP grafted with amide (OCP-A)	soluble	gel
Polybutadiene(PB)	insoluble	soluble
Polyisoprene (PIP)	soluble	soluble
Styrene-butadiene copolymer (SB)	insoluble	soluble
Ethylene/vinyl acetate copolymer (EVA)	insoluble	soluble
Ethylene/methyl acrylate copolymer (EA)	insoluble	soluble
Styrene/ethylene/butylene copolymer (SEBCP)	soluble	soluble

In the solubility test, polymer was mixed in oil at 180°F for 2 days.

- **The solubility of polymers in base oil varies with chemical structure of oil.**
- **The double bonds and polar groups (such as ester or amide) in polymers make it more soluble in vegetable oil.**
- **The gel of amide grafting OCP in vegetable oil is due to the formation of the hydrogen bonding in the solution.**

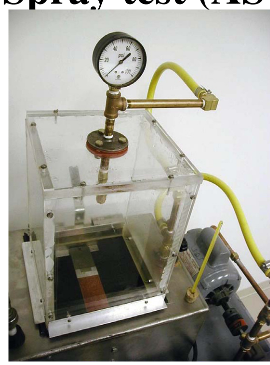
Experiment

Procedures:

NLGI #2 lithium grease + Polymer (liquid, powder, pellet, etc.) → Mixing at 230ºF for 2-3 hrs, then cool down → Polymer enhanced grease

Tests:

- ❑ **Water Spray test (ASTM D4090)**



Without polymer **With 1% PIP**

Before spray

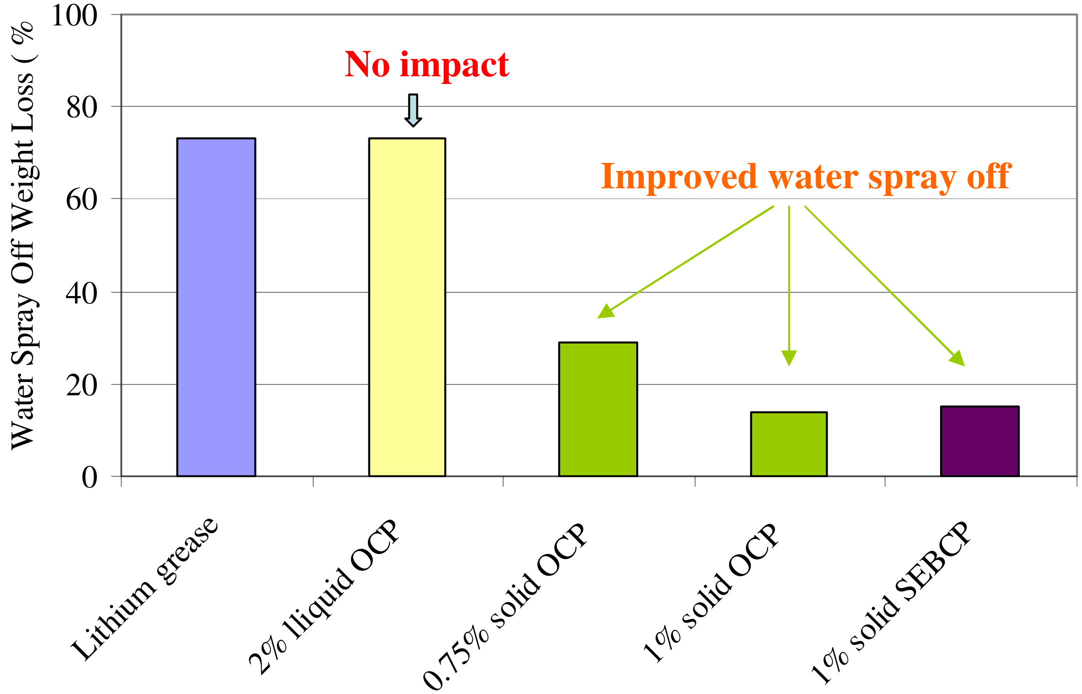
After spray

- ❑ **Shear stability-effect of 10,000 double strokes on cone penetration (ASTM D217)**

Results and discussions

Effect of polymer additives on mineral oil-based lithium grease

❑Water spray test (ASTM D 4090)

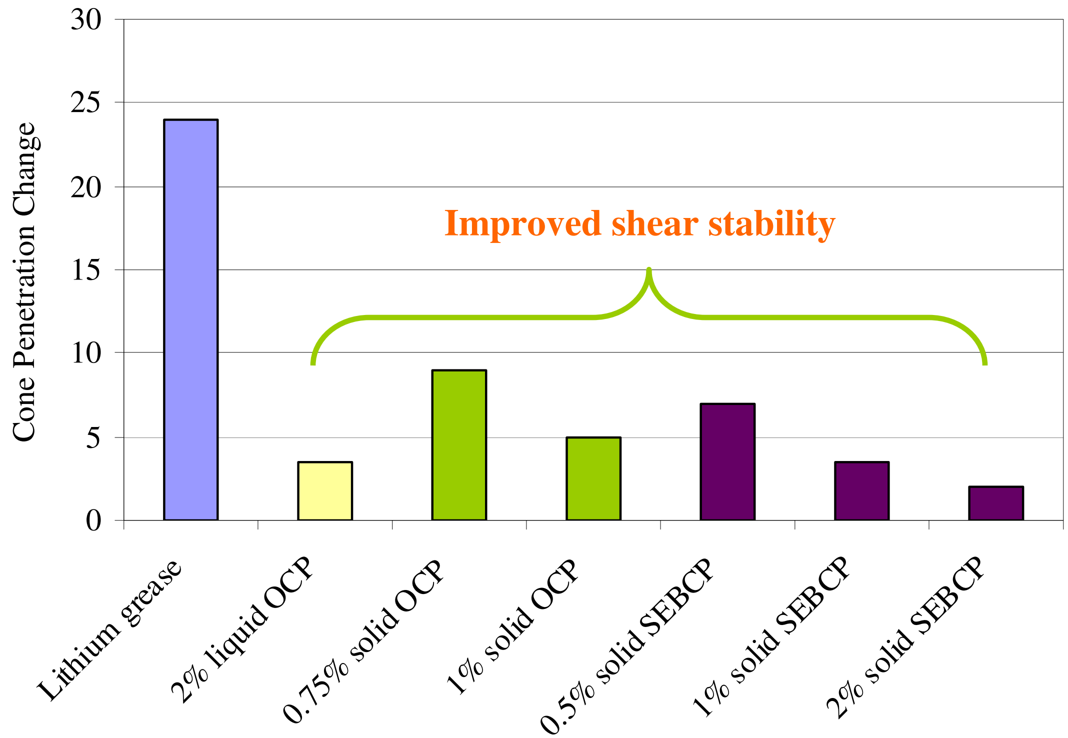


❑**Liquid OCP is 100% amorphous (no crystalline phase).**

❑**Solid OCP is semi-crystalline material with multiphase structure (amorphous phase and crystalline phase).**

❑**SEBCP is block polymer with polyolefin block and polystyrene block (the solubility of polystyrene block is very temperature sensitive and it has much less solubility in oil at temperature at temperatures below 60^{0}C).**

❑Shear Stability- Effect of 10,000 double strokes on Cone Penetration (ASTM D 217)



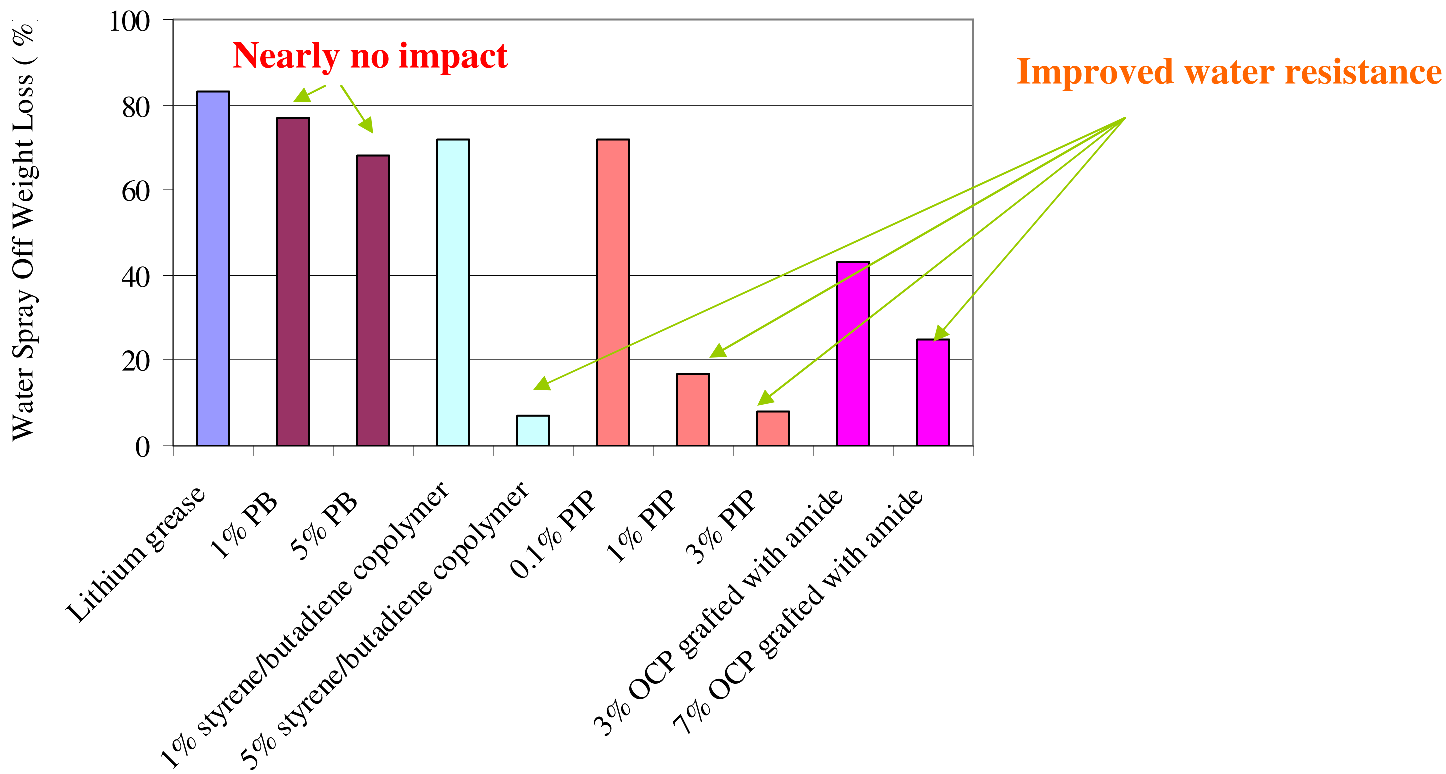
❑All the polymer used here improved the shear stability of lithium grease.(even polymer without networking can improve the shear stability)

❑The shear stability increases as the polymer concentration increases.

❑The consistency change of grease after long time shearing is associated with the break-up of the physical association of soap thickener. Compared with soap thickener, the chemical bonding in the polymer long chain is harder to break up. Therefore, polymer can improve the shear stability of grease.

Effect of polymer additives on the vegetable oil-based lithium grease

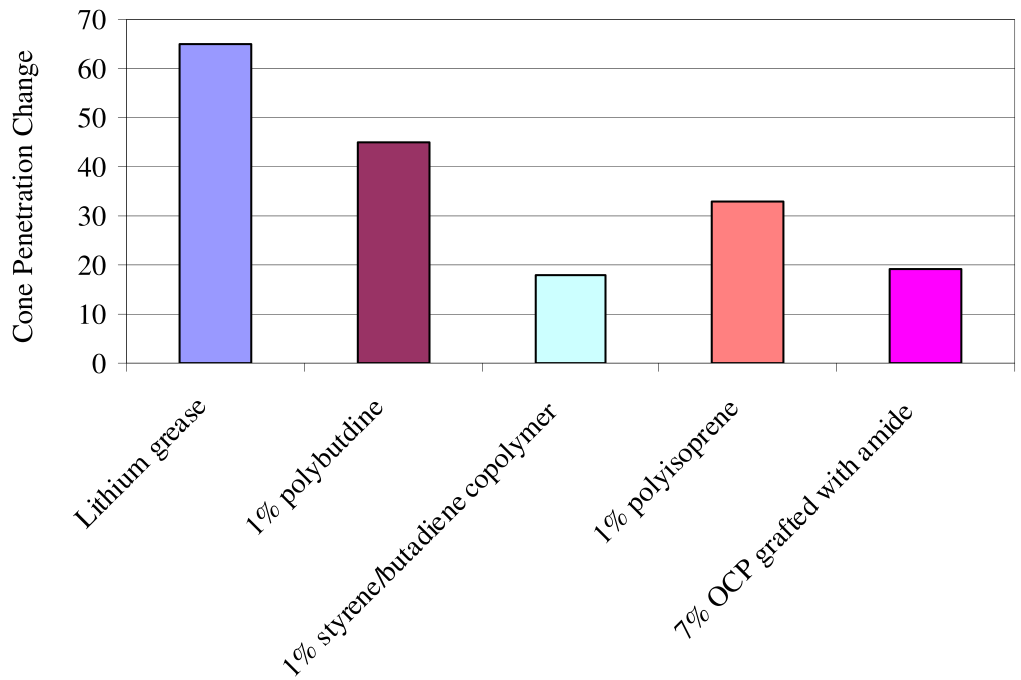
❑Water spray test (ASTM D 4090)



❑**PB has nearly no impact on the water resistance of grease.**

❑**SBR, PIP and amide grafting liquid OCP can improve the water resistance of grease significant at certain treating rate.**

❑<u>Shear Stability- Effect of 10,000 double strokes on Cone Penetration (ASTM D 217)</u>



❑**All the polymer used here improved the shear stability of lithium grease.**

❑**The shear stability increases as the polymer concentration increases.**

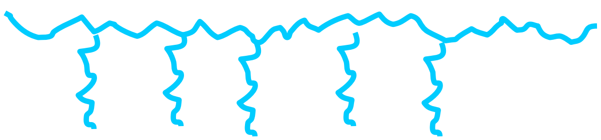
Conclusions

- **A selection of polymers with different structures were incorporated into two different types of lithium grease: mineral oil-based and vegetable oil-based. The water spray test (ASTM D4090) and shear stability test (ASTM D217) were used to evaluate the effect of polymer additives on the properties of grease.**
- **Due to the chemical structure difference between mineral oil and vegetable oil and the compatibility of polymer with oils, the performance of certain polymers in particular grease varies significantly.**
  - Semi-crystalline OCP and SEBCP can significantly improve the water resistance of mineral oil based grease. *By adding 1% of solid OCP, the weight loss percentage of grease decreased from 73% to 15%.*
  - PIP,SBR and amide grafting OCP can improve the water resistance of vegetable oil based grease. *By adding 1% of PIP the weight loss percentage of grease decreased from 83% to 17%.*
  - All the polymer used in this study showed positive result in improving the shear stability of grease.
- **The improvement of the water resistance performance after adding polymer was the result of forming interpenetrating networks by polymer and soap thickener.**
- **The improvement of shear stability after adding polymer was the result of the long chain nature of polymer.**

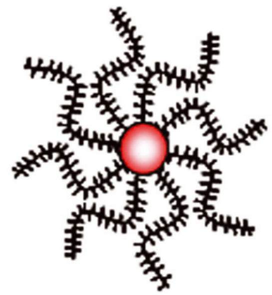
Future work

❑Using biopolymer or biodegradable polymer to enhance bio-based grease.

❑The effect of polymer architectures(like branch polymer or star polymer, etc.) on its performance in grease.



Branch polymer

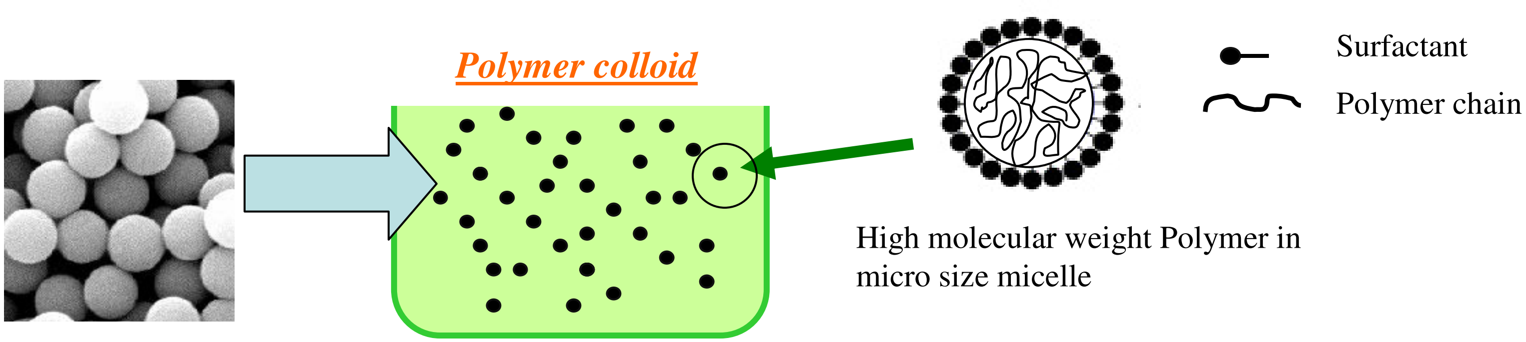


Star polymer

❑Exploring a more economic and efficient method to incorporate polymer in grease.

(It is difficult to mix high molecular weight solid bulk polymer into grease in short time. High molecular weight polymer suspended in liquid form is an alternative approach. The solvent is evaporated during heated mixing.)

Example: highly concentrated polymer colloid



Viscosity modifier for Synthetic esters

Kinematic viscosity of synthetic ester with 1% of Functional Products viscosity modifiers

Synthetic ester type	Chemical name	Kinematic viscosity of synthetic ester, cSt		VI	Pour point °C	Kinematic viscosity of synthetic ester with viscosity modifiers, cSt					
						1% V-508S		1% V-510S		1% V-515S	
		40°C	100°C			40 °C	100° C	40 °C	100 °C	40 °C	100 °C
Adipate ester	Di-tridecyl adipate	27	5.4	136	-57	46.6	8.2	32.7	6.4	42.3	8.8
Phthalate ester	Di-isodecyl phthalate	38	5.4	62	-42	81.7	9.5	70.2	9.4	64.0	9.2
Trimellitate ester	Tri-isodecyl trimellitate	124	11.9	81	-36	241.2	19.8	177.7	17.4	222.5	20.3
Polyol ester	C6, C7, C8 polyol ester	25	5	130	-60	44.3	7.8	N/A	N/A	N/A	N/A
Trimethylopropane ester (TMP)	trimethylopropane tricaprylate	20	4	140	-51	33.7	7.4	24.2	6.5	N/A	N/A

N/A : not compatible