

**Polymers in enhancing water spray off performance of mineral
oil and vegetable oil-based grease**

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Abstract

Adding polymer into grease can significantly enhance its properties like consistency, water resistance and shear stability. In this work, a selection of polymers with different structures was studied with the objective of in improving the water spray off properties of grease. Two types of lithium grease were used: mineral oil-based and vegetable oil-based. It is found that by adding 1% of a high molecular weight polyisoprene in vegetable oil-based grease, the weight loss percentage of the grease in water spray test decreased from 83% to 17%; and by adding of 1% of an ethylene/propylene copolymer in mineral oil-based grease, the weight loss percentage decreased from 73% to 15%. The water resistance improvement after adding polymer is due to the formation of the interpenetration networks (IPNs) by polymer and soap thickener. The polymer network can be formed by the physical crosslinking via crystalline phase, less soluble hard phase, hydrogen bonding, or by the long chain entanglement. Due to the chemistry difference between mineral oils and vegetable oils, the compatibility of polymer with base fluid varies as a result of its chemical structure. Therefore, their performance in grease varies with the base fluid of the grease.

1. Introduction:

Lubricating grease is a semisolid lubricant. It is used in specialized lubrication applications such as roller bearings and slow speed gear systems, where the liquid lubricant fails. The grease has both liquid phase and solid phase. The solid phase holds the liquid base fluid in the structure to provide the structure integrity. Under working condition, the lubricant fluid in the grease is released to perform lubrication. When the shear condition is removed the grease resumes back to semisolid state. There are three components in the grease: base lubricant fluid, thickener, and additives. The liquid lubricant in grease is immobilized by the network structure formed by thickener or solid particles like inorganic clay or other filler.^{1,2}

The thickener in grease provides the gel like network structure. The normal soap thickeners are metallic salts of long-chain fatty acids. In soap molecule, the ionic group is hydrophilic and the fatty hydrocarbon long chain is hydrophobic. The interactions between the ionic groups of different soap molecules and the interactions of the fatty hydrocarbon chain of the soap molecules help to form interlocked fibrous

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structures. Adding polymer to the grease can further enhance the grease properties such as improved consistency, better shear stability, enhanced water resistance, greater adhesion, elevated tackiness, and higher yield.³ Polymers with different chemical structures such as polyethylene, polypropylene, polyisobutylene, halogenated polyethylene, polymethacrylate, polyurea, polycarbonhydrates etc. are reported to be used to improve the lubricant.^{1,4,5} Authors tested the performance of a variety of polyolefin with different functional copolymer blocks such as styrene, acetate, acrylic, amide.

Water resistance of grease is an important property for grease used in an environment with water exposure. The water contamination of grease not only can diminish the greases' lubrication capability, but may also lead to washout or loss of rust and corrosion protection. ASTM D4049 is a standard test method determining the resistance of lubricating grease to water spray. This test determines how much grease will be removed when water is sprayed on it. Grease with low consistency or poor adhesion tends to experience high weight loss percentage under water spray. Adding high molecular weight polymer in lubricant can significantly increase the base oil viscosity. But 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.³ The grease fiber network entangles with the polymer network and forms flexible and reversible interpenetration networks (IPNs). The IPNs structure can improve the water resistance effectively. In an addition, by using polymer with highly polar functional groups on the chain which can interact with the high polar end of soap thickener, the polymer network can interact with the network formed by the soap thickener.

The compatibility between polymer and the lubricant oil in grease is another key factor determining the performance of polymer additives in grease. The base fluids come from different resources such as petroleum-derived chemicals (e.g. mineral oil), synthetics (e.g. synthetic ester, synthetic ether, silicones) and extraction from plants or animals. Mineral oil is a liquid hydrocarbon byproduct of the distillation of petroleum from crude oil. It can be classified as paraffinic oils based on α -alkanes, naphthenic oils based on cycloalkanes and aromatic oil based on aromatic hydrocarbons.¹ Alkanes are saturated hydrocarbons with linear or branched structures as in *Figure 1*(a) and (b). Cycloalkanes are saturated hydrocarbons containing five- or six- member cyclic rings as in *Figure 1*(c). Aromatic hydrocarbons contain conjugated aromatic rings as in *Figure 1* (d). Bio-based and biodegradable base oils are eco-friendly alternatives to petroleum-based products. Biodegradable products can reduce the negative environmental impact from leaks and spills. They are renewable and reduce the dependence of nonrenewable petroleum resources.¹⁻² Currently, the biodegradable base fluids are low molecular weight PAO, synthetic ester, synthetic ether, vegetable-based fluid, etc.⁶ Vegetable oil is one of the major bio-based base stocks for lubricant. Chemically, mineral and vegetable oils have significant structural difference. Mineral oils are hydrocarbons as shown in *Figure 1*. The major component

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in vegetable oils is triglycerides, which is an ester derived from glycerol and a mixture of different saturated and unsaturated fatty acids as illustrated in Figure 2. For example, the major unsaturated fatty acids in soybean oil triglycerides are alpha-linolenic acid, linoleic acid and oleic acid. The saturated fatty acids are stearic acid, palmitic acid, etc.^{7,8} The ester structure and the unsaturated double bonds make vegetable oil biodegradable. The polymers used for mineral oil-based grease do not work very well in vegetable oil-based grease due to the compatibility issue. Although there are several factors determining the solubility of polymer in the base fluid, certain structure and polarity similarities between the polymer and the base fluid are essential.

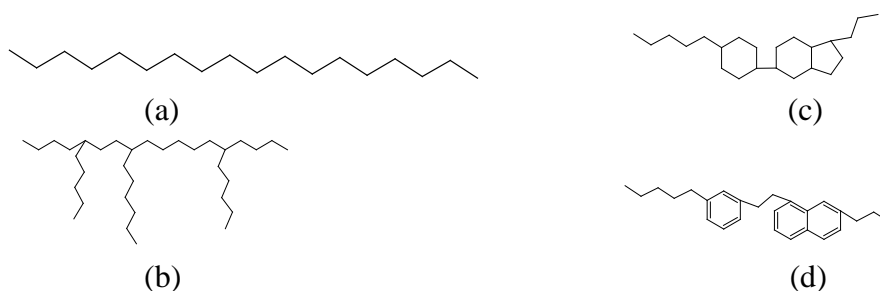


Figure 1 Chemical structure examples of different mineral oil (a) linear alkane, (b) branched alkane, (c) Cycloalkanes with alkane chain, and (d) aromatics with alkane chain.

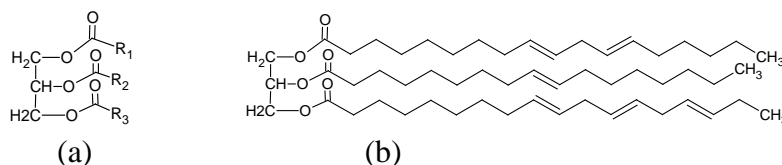


Figure 2 Chemical structures of (a) triglyceride (R1, R2 and R3 represent different unsaturated and saturated hydrocarbon chains) and (b) an example of triglyceride: an unsaturated fat triglyceride from etherification of glycerol with linoleic acid, oleic acid and alpha-linolenic acid.

In this paper, a selection of homopolymer, copolymer and block polymer was used to enhance the performance of two different types of NLGI#2 grade lithium grease: a mineral oil-based and a soybean-based. The water resistance and the shear stability of grease with polymer additives were evaluated by water spray test and worked cone penetration. The relationship of polymer structure with its effect on the performance of grease was studied.

2 Experimental:

2.1 Material and preparation

Both the mineral oil-based and the soybean-based lithium greases are NLGI #2 grade. The polymers used in this study and their structure are summarized in Table 1. The compatibility of polymer with grease varies from the chemistry of the base fluid. The solubility of polymers in base oil was tested before incorporating the polymer in

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the grease. In the solubility test, 0.5 g of polymer was added into 10g of ISO22 mineral oil and soybean oil respectively, and then the solution was heated to around 80°C and stirred for 2 days to ensure the polymer has sufficient time to dissolve.

In the process of incorporating polymers into the greases, the grease was heated and the additives were mixed in using medium speed on a Hobart model C-100 mixer. Polymer additives used in this study are in forms of crumb and liquid depending on their chemistry and molecular weight. Solid state polymers were mixed for about 2-3 hours and at 110°C temperature to ensure their dissolving in grease. Liquid state polymers were mixed for one hour.

Table 1 List of polymers used in experiment and their chemical structure

Polymer	Structure
Ethylene/propylene copolymer (OCP) (Saturated hydrocarbon)	$\left[\left(\text{CH}_2-\text{CH}_2 \right)_x \left(\text{CH}_2-\underset{\text{CH}_3}{\text{CH}} \right)_y \right]_n$
Polyisobutylene (PIB) (Saturated hydrocarbon)	$\left[\text{CH}_2-\underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}} \right]_n$
Polybutadiene(PB) (unsaturated hydrocarbon)	$\left[\begin{array}{c} \text{CH}_2 \quad \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{H} \end{array} \right]_n$
Polyisoprene (PIP) (unsaturated hydrocarbon)	$\left[\begin{array}{c} \text{CH}_2 \quad \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H}_3\text{C} \quad \text{H} \end{array} \right]_n$
Styrene-butadiene copolymer (SBR) (unsaturated hydrocarbon with rigid and less soluble styrene)	$\left[\left(\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2 \right)_x \left(\underset{\text{C}_6\text{H}_5}{\text{CH}}-\text{CH}_2 \right)_y \right]_n$
Ethylene/propylene copolymer grafted with amide (OCP-A) (saturated hydrocarbon with polar amide group on the side chain)	$\left[\left(\text{CH}_2-\text{CH}_2 \right)_x \left(\text{CH}_2-\underset{\text{CH}_3}{\text{HC}} \right)_y \left(\underset{\text{NH}}{\text{C}}=\text{O} \right)_z \left(\underset{\text{NH}}{\text{C}}=\text{O} \right)_n \right]_n$
Styrene-ethylene-butylene copolymer (SEBCP) (saturated hydrocarbon with rigid and less soluble styrene)	$\left[\left(\text{CH}_2-\underset{\text{C}_6\text{H}_5}{\text{CH}} \right)_x \left(\text{CH}_2-\text{CH}_2 \right)_y \left(\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2 \right)_z \right]_n$
Ethylene/vinyl acetate copolymer (EVA) (saturated hydrocarbon with polar ester group of vinyl acetate)	$\left[\left(\text{CH}_2-\text{CH}_2 \right)_x \left(\underset{\text{O}}{\text{HC}}-\text{CH}_2 \right)_y \right]_n$ $\begin{array}{c} \text{C}=\text{O} \\ \\ \text{CH}_3 \end{array}$
Ethylene/methylacrylate copolymer (EA) (saturated hydrocarbon with polar ester group of methylacrylate)	$\left[\left(\text{CH}_2-\text{CH}_2 \right)_x \left(\underset{\text{C}=\text{O}}{\text{HC}}-\text{CH}_2 \right)_y \right]_n$ $\begin{array}{c} \text{O} \\ \\ \text{CH}_3 \end{array}$

2.2 Measurement

2.2.1 Worked cone penetration

Worked cone penetration measurements were made in accordance with ASTM D 217, “Standard Test Method for Cone Penetration of Lubricating Grease.” With the sample and equipment at 25 °C, the sample was placed into the worker cup and subjected first to 60 and then to 10,000 double strokes in a Mechanical Grease Worker as shown in Figure 3. Cone penetration measurements were determined by using penetrometer as shown in Figure 4. The changes between worked 60 and 10,000 strokes of tested greases were evaluated.

2.2.2 Water spray off test

Water resistance of the grease samples was determined using ASTM D 4049, “Standard Test Method for Determining the Resistance of Lubricating Grease to Water Spray.” This test provides a realistic determination of how much grease will be removed when water is sprayed on it. Panel weights were determined to the nearest 0.1 g and after a 0.8 mm (1/32 in.) thick film of grease was applied to the panels they were reweighed. Any grease outside the scribe lines was removed before reweighing. The panels were inserted into the holders and then into the water spray apparatus as shown in Figure 5. The panel was centered below the spray nozzle. Water at 40 °C was sprayed at a pump pressure of 276 kPa (40 psi) onto the panel for 5 minutes. Grease outside the scribe lines was removed, and the panels were dried in an oven for 1 hour at 60 °C and reweighed. The percent grease weight loss was reported as the percent water spray-off.



Figure 3 mechanical Grease Worker



Figure 4 Penetrometer



Figure 5 Water spray test setup

3. Results and Discussions

3.1 Solubility of polymers in the base fluids of grease

The compatibility between polymer additive and base fluid of grease is essential to its performance. Table 2 lists the solubility of polymers in paraffinic oil and soybean oil. Polymers like Ethylene/propylene copolymer (OCP), ethylene/propylene copolymer grafted with amide (OCP-A), polyisobutylene (PIB) and can gradually dissolve in paraffinic oil, but their solubility in soybean oil is poor. This is due to the chemical difference between mineral oil and the triglyceride structure of vegetable oil. It requires certain structure and polarity similarity between polymer and the base fluid to achieve compatibility.

The saturated hydrocarbon structure of these polymers makes them have good affinity to saturated hydrocarbon paraffinic oil. Polymers like polybutadiene (PB), polyisoprene (PIP), Ethylene/vinyl acetate copolymer (EVA), Ethylene/methyl acrylate copolymer (EA) can dissolve in soybean oil, but are hard to dissolve in paraffinic oil. The double bond and the polar ester group in these polymers make them have good affinity to vegetable oil. Styrene/ethylene/butylene copolymer can dissolve in both paraffinic oil and soybean oil.

Table 2 Solubility of polymer additives in the mineral oil and soybean oil

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

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3.2 Polymer additives in mineral oil-based grease

Among all the polymers listed in *Table 1*, liquid OCP, semi-crystalline solid OCP, liquid PIB and solid SEBCP were successfully mixed in the grease to form a homogenous mixture. In some applications grease is exposed to water occasionally. Water contamination can change the properties of grease such as consistency, loss of adhesion, loss of rust and corrosion protection. Adding polymer into lubricant grease can improve its resistance to water spray. Water spray test is a method to evaluate the ability of grease to adhere to metal panel when subjected to direct, intense water spray. Shear stability of its consistency is another important property of grease. The crystalline and fiber structure formed by soap thickener in grease can be partially broken down under shear over time and cannot recover in a short time, which makes the grease softer. In this study, the shear stability of grease with polymer additives were evaluated by worked cone penetration. The cone penetration change of samples between work 60 and 10,000 strokes is a quantitative measurement of shear stability.

Figure 6 shows weight loss percentage of mineral oil-based lithium grease samples with different polymer additives after water spray. Adding polymer in grease dramatically increases the water resistance of grease. The weight loss of the lithium grease without adding polymer is 73%. Liquid OCP used in this study is amorphous and the solid OCP is semi-crystalline (some ethylene chain in OCP forms crystalline structure). It was found that 2% liquid OCP has no impact on the water resistance of the grease. However, the weight loss of grease with solid OCP decreased as the polymer loading increased. By adding 0.75% and 1% of solid OCP in the grease, the weight loss of grease decreased to 29% to 14%, respectively. This can be explained by the morphological structure difference between liquid OCP and semi-crystalline OCP. The crystalline phase in solid OCP acts as physical crosslink and helps the formation of the polymer network in the grease. The amorphous liquid OCP does not have such structure. Similar result was found in grease sample with SEBCP. By adding 1% of SEBCP in the grease, the weight loss percentage decreased to near 14%. In SEBCP, the styrene blocks have poor solubility in base oil. They form hard micro-gel domain in grease, which provides physical crosslinking for the polymer network.

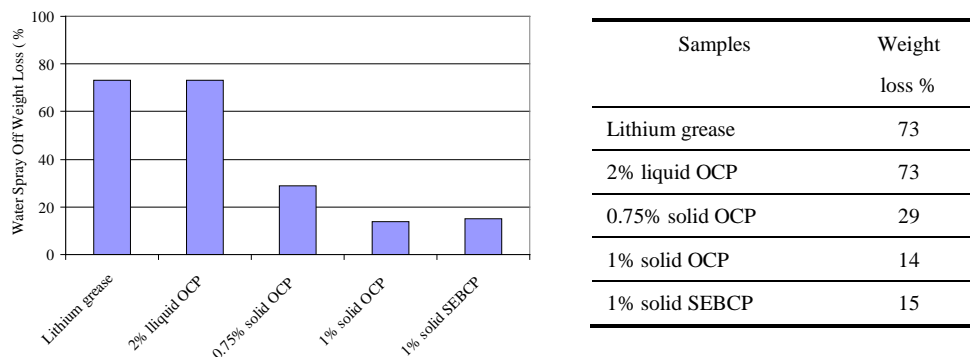
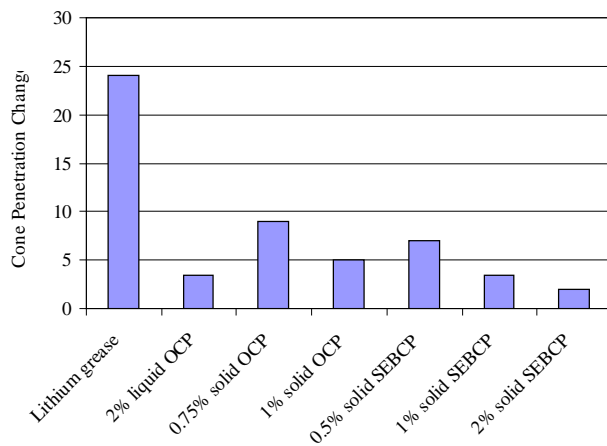


Figure 6 Water spray test, ASTM D 4090, mineral oil-based lithium grease sample with different polymer additives³

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Figure 7 shows the shear stability of grease with polymer additives represented by cone penetration change after 10,000 double strokes. It was found that adding polymer to the grease significantly increased the shear stability. The controlled grease sample had a worked cone penetration of 296 after 60 double strokes and penetration of 320 after 10,000 double strokes. A total of 26 cone penetration change. The unit of cone penetration is 1/10 mm. After adding 2% liquid OCP, the cone penetration change of grease decreased to less than 5. After adding up to 2% solid OCP and SEBCP, the cone penetration change decreases to less than 10. As the polymer loading increased, the cone penetration change decreased. By comparing Figure 7 with Figure 6, an interesting phenomenon was observed that the liquid OCP did not improve the water resistance of grease, but increased the shear stability of grease. In terms of enhancing the shear stability of grease, the polymer does not have to form network in the grease. The fiber structure of soap thickener in grease is formed by the physical bonding of soap molecules. It can be partially dissociated under long time shearing and it takes time for the soap molecule to reassemble back to its original state after the shearing is removed. The polymer chain length is much longer than the fatty chain of soap. The polymer chain is formed by chemical bonding which is harder to break down under moderate shear than the physical bonding unless the polymer chain is very long.



Samples	Penetration change
Lithium grease	24
2% liquid OCP	3.5
0.75% solid OCP	9
1% solid OCP	5
0.5% solid SEBCP	7
1% solid SEBCP	3.5
2% solid SEBCP	2

Figure 7 Shear Stability- Effect of 10,000 double strokes on Cone Penetration (ASTM D 217), mineral oil- based lithium grease sample with polymer additives³

3.3 Polymer additive in soybean-based grease

Due to the chemical structure difference between mineral oil and vegetable oil, the polymers like OCP, PIB does not dissolve in grease. In this study, PBR, PIP, SBR, EVA, EA, liquid OCP grafted with amide were used in soybean-based lithium grease. Liquid OCP grafted with amide is formed by reacting maleic anhydride grafted OCP with mono ethanol amine. Grafting the amide groups on OCP introduce hydrogen bonding sites in the polymer. Although EVA and EA are soluble in vegetable oil, they dissolve in grease very slowly at 100°C.

Figure 8 shows a photo of the water spray sample (Fig. 8. a). The grease sample without polymer is almost washed off after water spray (Fig. 8. b), while the grease with 1% of PIP is nearly unchanged after water spray (Fig. 8. c). Figure 9 shows the weight loss of the grease sample with polymer additives after water spray. The weight loss of grease sample without polymer is 83%. Only very minor water resistance improvement was observed after adding up to 5% PBR due to lack of physical crosslink for the polymer network. By adding 5% SBR, the weight loss decreased to 7%. The less solubility styrene block forms micro-gel, which acts as physical crosslink. The grease sample with 3% of PIP has weight loss below 10%. The PIP used in this study has very high molecular weight, which can easily entangle together and form a network. OCP cannot dissolve in vegetable oil. OCP grafted with amide group (OCP-A) forms liquid gel in soybean oil. By adding 3% of OCP-A and 7% of OCP-A, the weight loss of grease decreased to 43% and 25%, respectively. In the previous section, it was mentioned that liquid OCP has nearly no impact on the water resistance of grease due to lack of polymer network. However, after grafted with small amounts of amide, it demonstrated positive improvement on the water resistance of grease. The amide groups form hydrogen bonding, which acts as physical cross linking for the polymer network. In addition, due to its low molecular weight (short polymer chain length) compared with solid OCP, the liquid OCP-A requires higher polymer loading in the grease to build the network. Similar to the results in mineral oil-based grease, adding polymer in vegetable-based grease also improved the shear stability of the grease as shown in Figure 11.

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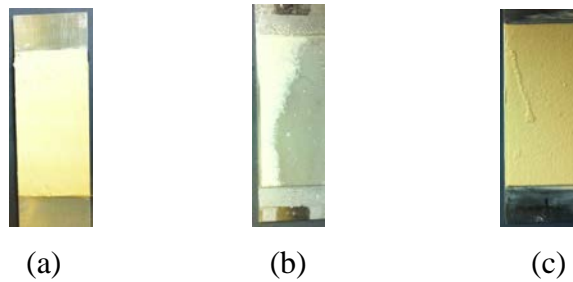
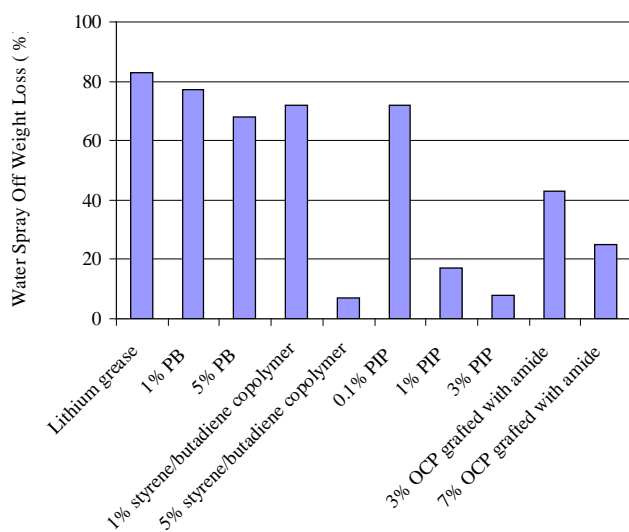
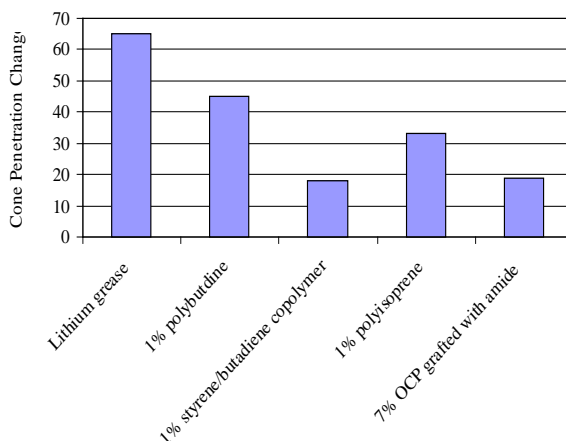


Figure 8 Photos of grease sample on the metal plate (a) before spray (b) after water spray (control soybean-based lithium grease without polymer) (c) after water spray (soybean-based grease with 1% PIP)



Samples	Weight Loss %
Neat Lithium grease	83
1% PB	77
5% PB	68
1% SB	72
5% SB	7
0.1% PIP	72
1% PIP	17
3% PIP	8
3% OCP grafted with amide	43
7% OCP grafted with amide	25

Figure 9 Water spray test, ASTM D 4090, vegetable-based lithium grease sample with different polymer additives



Samples	Penetration change
Lithium grease	65
1% polybutdine	45
1% SB	18
1% polyisoprene	33
7% OCP grafted with amide	19

Figure 10 Shear Stability- Effect of 10,000 double strokes on Cone Penetration, ASTM D 217, soybean-based lithium grease with different polymer additives

3.4 Mechanism

The results above showed that the existence of polymer network structure did improve the water resistance of grease. This network can be formed through different approaches such as by the physical crosslinking via crystalline phase (e.g. semi-crystalline OCP) and less soluble hard phase (e.g. SEBCP and SBR); by the hydrogen bonding (e.g. amide grafting OCP) or by the long chain entanglement (e.g. high molecular weight PIP). The fiber network structure formed by soap thickener in grease is reversible. In the mixing process, the network formed by soap thickener is partially dissociated under heating. After cooling down, soap thickener resumes to its fiber structure with the presence of polymer network. These two networks interpenetrate with each other. The interpenetrating networks (IPNs) with polymer and the soap thickener are formed as illustrated in Figure 11.

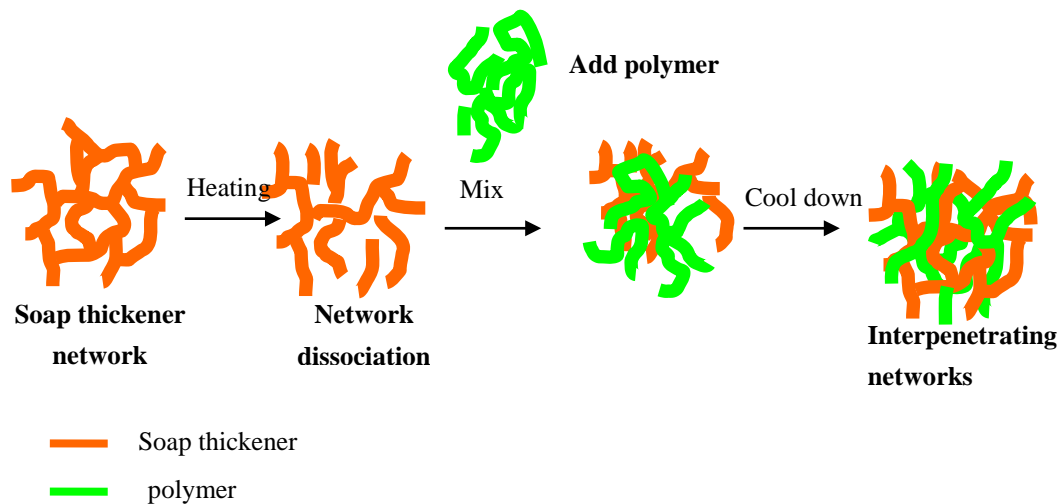


Figure 11 Illustration of the interpenetrating networks (IPNs) formed by polymer and soap thickener.

4. Conclusions

A selection of polymers with different structures was incorporated into mineral oil-based grease and soybean-based grease. It was found that semi-crystalline OCP and SEBCP can significantly improve the water resistance of mineral oil-based grease, but they do not work for soybean-base grease. PIP, SBR and amide grafting OCP work well in improving the water resistance of soybean-based grease. By adding 1% of a high molecular weight polyisoprene in a vegetable oil-based grease, the weight loss percentage of the grease in water spray test decreased from 83% to 17%. By adding of 1% of an ethylene/propylene copolymer in a mineral oil-based grease, the weight loss percentage decreased from 73% to 15%. The improvement of the water resistance performance after adding polymer was the result of the forming interpenetrating networks by polymer and soap thickener together. All the polymers used in this study showed positive results in improving the shear stability of grease.

5 Acknowledgements

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