

Friction modifiers: Study of an inverse relationship between engine efficiency and wear

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Introduction

In the pursuit of achieving improved fuel economy and/or increased engine power, several advancements with engine oils to improve engine efficiency have surfaced. The most prominent example is work done to reduce internal friction (or traction) of an engine lubricant by reducing apparent viscosity. While there is no theoretical limit to how thin an engine lubricant's viscosity can be to maximise efficiency, an engine has a theoretical limit for lubricant film thickness. Beyond that point, or too thin of a fluid film; premature wear and engine failure can occur. To address this problem, friction modifiers (FMs) have been employed to provide additional boundary lubrication preventing engine parts from contact, and reducing wear.

The importance of FMs has increased dramatically as engine lubricant viscosity and film thickness decreased in recent years to meet governmental regulations on OEM fleet fuel efficiency. FMs can permit use of lower viscosity engine lubricants to meet the needed engine efficiency requirements while managing or even enhancing engine durability.

This review will discuss the current state of engine oil friction modifiers, advancements into different classes of modifiers, their current applications, outcomes of use, and future projections for these modifiers.

Classes of FMs and how they are applied

Organic friction modifiers (OFMs)

Friction modifiers can be divided into several classes; these include organic friction modifiers, inorganic friction modifiers (iOFMs), and functionalised polymers [2]. Structurally, organic friction modifiers (OFMs) have an amphiphilic molecular structure, like a cell membrane Polar heads of this structure allow preferential migration toward polar surfaces (i.e., metal). Figure 1 introduces typical OFM structure for a friction modifier. Depending on how densely packed the modifier is, variations in friction coefficients will exist [3]. Amphiphilic structure in additives is key to OFM structure since nonpolar forces allow the structure to retain shape, allowing the OFM to slide across surfaces. Primarily with metal surfaces, anti-friction properties work upon adsorption to the surface; in this case, engine surfaces [4]. OFMs

generally have temperature limits and will lose effectiveness in friction prevention once said limits are reached. In this case, the mode of failure would be reaching such extreme conditions, such as high temperatures, where the engine would most likely fail as well. Also, recent research has indicated that OFMs have a pressure limit, where monolayers of OFMs are so tightly packed that structural collapse occurs, rendering the material useless [3,4]. Examples of common OFMs include glycerol mono-oleate (GMO) and oleyl amide. Specifically, glycerol mono-oleate functions as a friction modifier via hydrolysed into oleic acid and adsorption onto metal surfaces for lubrication [5]. It is widely used throughout the lubricant industry, with current studies observing its interactions with other friction modifiers and observing any synergies.

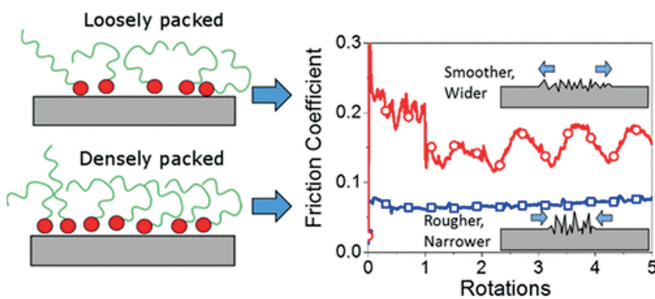


Figure 1: Typical OFM amphiphilic structure found throughout films [4]

Inorganic friction modifiers (iOFMs)

As for inorganic friction modifiers (iOFMs), they serve as the second of three classes of friction modifiers found throughout the engine lubricant industry. Like OFMs, they serve to reduce friction within engines, but with structure breakdown that leads to the formation of films that reduce shear stress [6]. Common elements included in iOFMs include molybdenum, sulphur, and phosphorus; this includes their respective benefits to lubricants discussed in later sections. Molybdenum, for example, shows promise as an alternative to OFM-enriched oils. Thicker protective films and higher contact potentials have indicated iOFMs based in molybdenum as promising

alternatives [6]. Providing thicker films decreases the chance of lubricant failure and mechanical wear. For contact potentials, molybdenum creates high contact potentials, which indicates a better formation of a film surface while under stress [6].

Other common elements used within iOFMs include Boron, Carbon (in the form of graphene/graphite), and Fluorine. Boron in iOFMs can come in the form of boric acid (H_3BO_3) as a solid lubricant, and notably borate derivatives in inorganic compounds [9]. While excelling in antiwear and temperature loading properties (able to withstand temperatures over $500^\circ C$), mechanisms for adhesion and lubrication are poorly understood by researchers [9,10]. With carbon-based additives, graphene as carbon nanotubes (CNTs) have shown promise. For graphene, interactions with Fe_2O_3 -based multi-walled CNTs showed excellent antiwear and friction reduction depending on the blend. As such, mass production capabilities are readily available and easy given current infrastructure, but accumulations in engines present a challenge for researchers [11]. Finally, fluorinated additives can present as powders, and PTFE shows promise due to reductions in friction. However, results from studies have indicated mixed results while in use.

Functionalised polymers as friction modifiers

The final class of friction modifiers falls under functionalised polymers (FPs). FPs are a class of OFMs used as an alternative to traditional friction modifiers. Within engines, functionalised polymers reduce friction primarily through bonding to polar surfaces, forming thicker films than traditional surfactants [13]. The polymeric structure also modifies the temperature-viscosity properties of the lubricant used for the engine, allowing for further friction reduction. Block copolymers, which include more than one monomeric species within a chain in a structured manner, further enhance adsorption on metal surfaces. Recent studies have examined the anchoring chemistry of functionalised polymers and their role in

changing the ordering of the final boundary layer for a lubricant [13]. Anchoring chemistry observes how a molecule binds to a surface; for this context, how lubricant molecules react with mechanical surfaces. Surface stability and shear stress rates also have direct influences from anchoring chemistry. Also, research has observed whether synergies between two friction modifiers are tribologically sufficient [13]. Increased friction modifier efficiency within functionalised polymers allows for the oil lifecycle to be extended, decreasing the need for engine oil to be disposed of. Such functionalised polymeric friction modifiers would be able to prolong the life of engine lubricants, as well as the life of the engine, by reducing friction.

Challenges, Intro to Synergies/Antagonisms

While friction modifiers of all classes exhibit great properties, certain challenges remain. This includes mixing with friction modifiers and their interactions with film thickness. For one, the increased use of low-friction engines in general has decreased the effectiveness of friction modifiers [15]. This has become paramount in finding “perfect” engine oils and lubricants. As such, the challenge of reducing friction in boundary and mixed lubrication blends, while retaining effectiveness over time, serves as a base for promising future research. Certain friction modifiers contain sulphur and phosphorus, which reduce the efficiency of catalysts within engines [16]. Current research has looked into OFMs as an alternative to traditional friction modifiers.

On top of these synergies involved, certain observed characteristics demonstrate antagonistic interactions between lubricants with friction modifiers and metal surfaces. These include corrosion, deposit formation, and decreasing antiwear performance. For corrosion, this involves the degradation of metallic surfaces due to repeated chemical exposure in conjunction with mechanical stress (i.e. friction over time). As for decreases in antiwear performance, one study implicated aminic dispersants as decreasing ZDDP’s

antiwear performance due to reducing ZDDP’s adsorption abilities [17]. In decreasing antiwear performance, engines suffer from increased wear and possible failure while in operation. In conjunction with increased friction performance, decreased antiwear performance presents an interesting challenge to this relationship. Both synergies and antagonisms such as these will be highlighted by this review.

Recent advancements and inverse relationship

OFMs and Organomolybdenum modifiers

Despite these challenges, friction modifiers remain imperative in reducing friction and energy losses. In the pursuit of efficient engine lubricants, an interesting trend forms: increased efficiency leads to thinning of the lubricant’s film thickness as well as engine wear. For example, when relating to crank angle and film thickness, there is a decrease in film thickness; Figure 2 below shows this relationship at different engine speeds [16]. While this is expected, the challenge for researchers is to improve film thickness while maintaining efficiency and minimising wear. This challenge is key to understanding the need for improved friction modifiers.

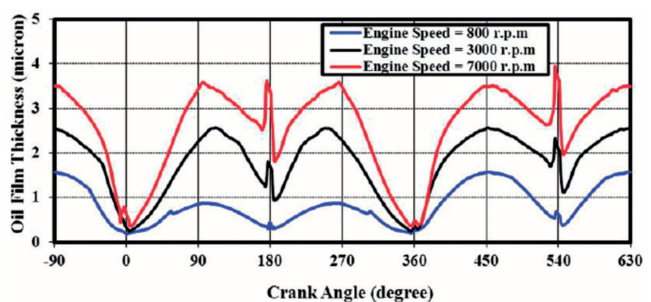


Figure 2: Relationship between engine speed on oil thickness between top ring and cylinder liner using SAE 20W40 oil [16]

Recent advancements have shown great progress within this field. In the pursuit of better friction modifiers, researchers have analysed several properties to develop optimal blends for a variety of uses. One area of research looks into improving low-friction engines and their efficiency while maintaining efficient fuel economy. Several studies have shown

advancements within this field. For OFMs, studies have noted the need for improvements within molecular structure to account for new changes [17]. The growing need for multi-faceted friction modifiers allows engines to be free of any possible issues. This includes promoting oxidative and anti-wear properties under certain conditions. As an engine undergoes combustion, exposure to water and high temperatures will degrade lubricants, leading to wear. Therefore, studies must look into friction modifiers as anti-wear and antioxidative additives to promote lubricant integrity while supplemented monofunctional friction modifiers are still used. Gatto et al. noted the anti-oxidative and wear properties working synergistically with other compounds during engine testing [18]. This interaction, observed between molybdenum and alkylated diphenylamines, proved that low concentrations of molybdenum within engine oil work as multifunctional. Although proper conditions and specific combustion rates are needed for each additive used, this study provides a base for how future research can work to improve synergistic relationships. Organomolybdenum friction modifiers also increase fuel efficiency and economy by nearly 1% [19]. Such an increase shows promise that friction modifiers hold for the future. As for this inverse relationship, modifying the chemical structure to synergise with other additives and knowing how it interacts with the engine surface will keep film thickness in check. Further research into organomolybdenum and molybdenum derivatives such as molybdenum dialkyl dithiocarbamate (MoDTC) shows that while effective as engine oils, their byproducts of molybdenum and sulphur degrade catalytic agents and automotive parts [20]. Therefore, the need for alternatives is imperative in the reduction of engine and lubricant wear.

In looking at alternative friction modifiers, oilless additives show promise in promoting excellent fuel economy for engines and maintaining traction reduction. Toyhama et al. observed certain

polymethacrylates (PMAs) as alternatives to traditional friction modifiers in oils [20]. For experimentation, researchers created PMAs of different molecular weights, each having a different number of dimethyl-amino-ethers (DMAE) attached to vary the quality of adsorption for experimentation. Results demonstrated a general decrease in friction coefficients with increasing sliding velocity, with the largest drops associated with PMAs of higher molecular weight and more DMAE groups. Figure 3 displays these results, with all groups following a similar downward trend [20]. Increased amounts of groups created stubborn films on interacting surfaces [20]; this property of lubricant thickness is imperative to observe the inverse relationship outlined earlier. Since these films are difficult to remove and effectively cover the engine surface material, this leads to decreased engine wear. Results also correlated increased functional groups with increased surface coverage for effective adsorption [20]. Further research must observe PMAs' synergies with other fuel additives, such as organomolybdenum modifiers and anti-wear agents, and various engine conditions for effective commercialisation.

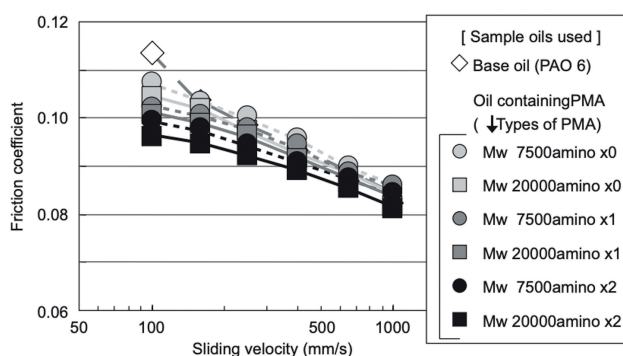


Figure 3: Friction reducing effects by PMAs introduction to various oils [20]

Along with observing PMAs as an alternative, synergies between organomolybdenum modifiers and OFMs have been studied for an improvement to overall engine efficiency, fuel economy, and oil performance. Wang et al. observed the tribological performance of organomolybdenum modifiers in

the presence of organic friction modifiers, such as glycerol monooleate and pentaerythritol [21]. The goal of this study was to determine the tribological and synergistic differences between sulphur-free, sulphur- and phosphorus-free molybdenum additives with OFMs. For testing, friction coefficients and engine wear on a model block-on-ring test ring were measured [21]. Also, interactions between these additives were observed to determine the most effective combination. Results indicated an increase in temperature with glycerol monooleate in MoDTC increased the friction coefficient, while N,N-Dimethylhexadecylamine and Pentaerythryol showed a dramatic decrease in coefficient. Also, all OFMs reduced material wear except in the BO-MA-PT formulation. Synergies for lubrication were best observed in the BO-MC-PT combination, which combined base oil with MoDTC and Pentaerythritol additives, compared to other additive combinations [21]. For applying these results to the inverse relationship between efficiency and thickness, low-friction coefficient results and anti-wear synergies indicate excellent results. However, creating lower friction oils through advanced friction modifiers can lower film thickness [22]. Future research should continue observing these synergies with an emphasis on how general friction modifier properties and their synergies affect film thickness. By preventing film thickness decline, there will be an increase in engine longevity and overall satisfaction for any application.

Functionalised Polymers

Functionalised polymers (FPs) have also been the subject of exciting advancements within tribological fields. Due to their molecular structure and observations in anchoring chemistry, functionalised polymers as friction modifiers have shown promising advancements for maintaining film thickness for engines. Advancements in ZDDP friction modifiers were seen in a study by Dawczyk et al., where they noted that an appropriate amine/functional group is imperative to friction reduction and their harmful

effects on ZDDP tribofilms [22]. Observations looked specifically at ethoxylated alkylamines OFMs working synergistically with ZDDP. Results from testing for friction coefficient and film thickness after ethoxylated alkylamines were combined to show any possible effects indicated that some boundary film is removed with a reduced friction coefficient. Ethoxy groups were shown to remove much of the ZDDP-tribofilm, but greatly increase friction [22]. Figure 4 below demonstrates this trend across several manufactured blends, along with surface roughness in nanometers [22]. As such, maintaining an optimal blend between ZDDP and the appropriate amount of ethoxylated alkylamines within friction modifier additives is paramount to future research. As it applies to the inverse relationship, an increase in ethoxylated alkylamines advances engine wear and, potentially, engine failure; combinations of both ethoxylated alkylamines and engine wear increase engine failure chances, given that the engine is used as intended. For synergies, the relationship between ZDDP and ethoxylated alkylamines Researchers also indicate that synergistic interaction between ethoxylated alkylamines and ZDDP indicates that their combination resulted in enhanced friction reduction and film thickness maintenance for engines. Such results prompt the formulation of lubricants and additives for low boundary friction and improved fuel economy.

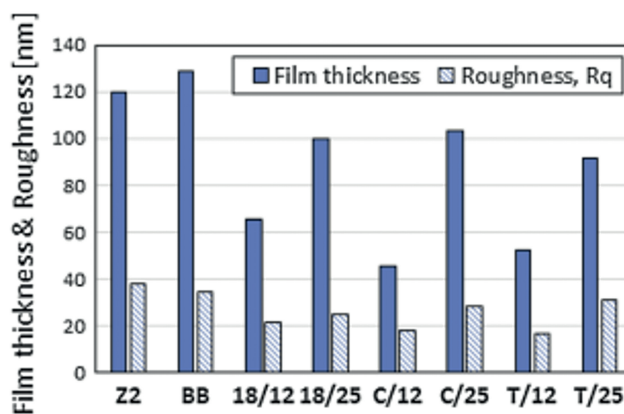


Figure 4: Change in ZDDP mean film thickness and roughness (nm) 3 hours after rubbing into surface with BB (base blend) and various OFM solutions [22]

Continuing with functionalised polymers, Hong et al. observed polymeric friction modifiers (Perfad XG 2500) combined with MoDTC and ZDDP at different temperatures to observe any tribological advancements [23]. Perfad XG 2500 is a relatively new polymeric friction modifier used for reducing friction throughout engines. In their results, researchers found that interactions between polymeric friction modifiers and this MoDTC/ZDDP decrease film thickness at higher temperatures, but the inherent properties of MoDTC and ZDDP allow the oil a prolonged service life and prevent wear over time. Also, researchers found that Perfad XG 2500 and MoDTC have synergistic effects and are optimal for antifriction applications, with reductions up to 20.83% [23]. More research into optimal ratios for adding oils must be conducted for replications of these results. For more alternatives to traditional friction modifiers, research into carbon nano-tubes has shown promise due to rising wear and increasing automotive engines. Carbon nanotubes may reduce friction due to their shape and optimal thermal conduciveness [24]. Further research is ongoing to better understand how graphene behaves mechanically and thermally when working in high-temperature environments as those found in engines. Earlier this year, researchers noted graphene's tribological properties while in liquid form and working together with several other friction modifiers. Enhanced properties include decreased wear on material surfaces and maintained film thickness when exposed to high temperature- a key component in this discussion on friction modifiers [25].

ZDDP

The inverse relationship between engine efficiency and engine wear for film thickness observed within the aforementioned studies provides a basis for improved research. The examples above provide insight into how synergistic effects, individual modifier characteristics, and temperatures modify their effectiveness. Film thickness varies by application,

operating conditions, and viscosity of the base oil used [26]. As such, friction modifier addition would alter base oil operating conditions through chemically modifying friction coefficient and viscosity. For maintaining film thickness throughout the engine and maintaining operating conditions, ZDDP alternatives are growing in popularity due to ZDDP by itself increasing friction and potentially harming catalytic converters which shortens engine lifespan [21,26]. However, AMSOIL has found that reducing ZDDP has been found to reduce effectiveness between certain high-pressure components for older engines, including high-tension valve springs, amongst others [28]. Alas, the need for maintaining proper ZDDP ratios is crucial in maintaining engine efficiency, longevity, and wear.

Film thickness

When addressing film thickness, Anghel et al. observed the characteristic behavior of certain friction modifiers between thick-film models for commercial applications [29]. Carboxylic acid and a dimer acid in hexadecane or mineral oil were used to form thick boundary films and demonstrated tribological properties; properties enhanced included forming boundaries 50-70 nm thick. However, such lubricants became either partially or wholly destroyed at high speeds, primarily above 0.08 m/s [29]. These conditions imply friction reduction at intermediate speeds for thicker oils; such results indicate certain industrial applications or older automotive engines. Applying these conditions to engine oils would be detrimental. Having film thickness decrease rapidly at high speeds, as in combustion engines, would immediately result in engine wear and destruction.

Volatility for friction modifiers plays a key role in engine oil's effectiveness while in use. Indeed, temperature conditions affect oil and additive properties, changing how they interact with surfaces. Volatility, or how quickly the oil evaporates during operating conditions, is correlated with film thickness. Low volatility oils are harder to evaporate while in

use due to strong bonding between large molecules, which makes it difficult for evaporation while under stress and inducing less volatility. This ensures that film thickness remains at certain levels to prevent engine wear [30]. Research into volatility and friction modifier relationships looks at these interactions to see how they affect the inverse relationship between efficiency and wear with film thickness. One study by Cañellas et al. observed the tribological properties of friction modifiers, along with anti-wear additives and esters, for electric vehicle applications [31]. As the future of the automotive industry, electric and hybrid vehicles require lubricants with friction modifiers to ensure minimal friction losses. Such oils would interact with gears and different clutches for vehicle speeds. Certain greases and oils, including polypropylene acting as a thickening agent, have shown friction modifier properties when converted in-situ [30,31].

Specifically for this study, Cañellas et al. tested how esters synergised with friction modifiers and/or anti-wear additives for a variety of tribological applications. Researchers tested for traction coefficient- a term analogous to friction modifiers- and saw a decrease between 20-50%, depending on the mixture used [31]. Testing methods included using a Mini-Traction Machine running for six hours while lubricant was covered onto a steel ball and allowed to roll over a metal disk. Friction modifiers used included MoDTP, OFM, and poly isobutyl succinate-polyetheramine polymer (PFM1) and another polymeric friction modifier designated as PFM2. Results indicated synergies for friction reduction between MoDTP and ZDDP via oxidative and reduction reactions, a reduction of traction coefficient by 64% compared to base PAO 6 oil, and a decrease in traction coefficient by 62% for PFM 2 [32]. Future research will continue to investigate these synergies, along with new formulations of engine oils.

Conclusion

In tribology, the pursuit of high-quality engines and

engine oils has called for maintaining film thickness. Tribological industries keep pushing the limits of engine technology with respect to improved power and performance. As such, improvements in engine oils (namely, friction modifiers) are required for a robust film thickness throughout a variety of operating conditions. Friction modifier additives, including OFMs, iOFMs, and functionalised polymers as friction modifiers, have all shown promise in reducing engine wear and friction. Researchers from across the world have experimented with different friction modifier mixtures to observe tribological synergies between each class, including friction modifier materials and chemicals. In this pursuit, an inverse relationship between engine efficiency and engine wear in relation to fuel economy further inclines researchers to investigate synergies for the best engine oil possible. Also, researchers' current findings indicate that further investigations are required for complete synergy understanding. Systematic combinations between FMs and their engine oils must be observed for advancing mechanical engine properties, with advancements required from the molecular level to validation levels once an engine is completed. As such, future research will further investigate synergies, ushering in a new age for tribology.

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Authors

Dr. Raj Shah serves in the role of Director at Koehler Instrument Company in New York, boasting an impressive 28-year tenure with the organisation. Recognised as a Fellow by his peers at eminent organisations such as IChemE, AOCS, CMI, STLE, AIC, NLGI, INSTMC, Institute of Physics, The Energy Institute, and The Royal Society of Chemistry, he stands as a distinguished recipient of the ASTM Eagle award. Dr. Shah, a veteran in the field, recently coedited the highly acclaimed "Fuels and

Lubricants Handbook," a bestseller that unravels industry insights. Explore the intricacies at ASTM's Long-Awaited Fuels and Lubricants Handbook 2nd Edition Now Available (<https://bit.ly/3u2e6GY>).

His academic journey includes a doctorate in Chemical Engineering from The Pennsylvania State University, complemented by the title of Fellow from The Chartered Management Institute, London. Dr. Shah holds the esteemed status of a Chartered Scientist with the Science Council, a Chartered Petroleum Engineer with the Energy Institute, and a Chartered Engineer with the Engineering Council, UK. Recently honored as "Eminent Engineer" by Tau Beta Pi, the largest engineering society in the USA, Dr. Shah serves on the Advisory Board of Directors at The Pennsylvania State University (The School of Engineering Design and Innovation), Farmingdale University (Mechanical Technology), Auburn University (Tribology), SUNY Farmingdale (Engineering Management), and the State University of NY, Stony Brook (Chemical Engineering/Material Science and Engineering).

In tandem with his role as an Adjunct Professor at the State University of New York, Stony Brook, in the Department of Material Science and Chemical Engineering, Dr. Shah's impact spans over three decades in the energy industry, with a prolific portfolio of over 625 publications. Dive deeper into Dr. Raj Shah's journey at <https://bit.ly/3QvfaLX>.

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Simultaneously, within the dynamic internship program at Koehler Instrument Company in Holtsville, Mr. Nicholas Douglas is a standout participant. He will soon graduate with a degree in Chemical Engineering at Stony Brook University, Long Island, NY, and has excelled in this competitive internship program.

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