TRIBOPOLYMERIZATION: AN ADVANCED LUBRICATION CONCEPT FOR AUTOMOTIVE ENGINES AND SYSTEMS OF THE FUTURE

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Abstract

Advanced lubrication technologies based on the concept of tribopolymerization as a mechanism of boundary lubrication are described. Advantages of this approach as well as potential applications which could have an impact on the design, manufacture, and performance of existing and future automotive engines are presented and discussed.

Tribopolymerization, a novel concept of molecular design developed by Furey and Kajdas, involves the continuous formation of thin polymeric films on rubbing surfaces; the protective films formed are self-replenishing. The antiwear compounds developed from this technology are effective with metals as well as ceramics and in the liquid as well as vapor phases. Furthermore, they are ashless and contain no harmful phosphorus or sulfur; and many are biodegradable. Thus, potential applications of this technology are diverse and include a variety of cost/performance/energy/environmental advantages.

Examples include the following: (a) machining and cutting applications using thin films to reduce friction and ceramic tool wear; (b) the lubrication of ceramic engines (e.g., low heat rejection diesel engines) or ceramic components; (c) the development of ashless lubricants for existing and future automotive engines to reduce exhaust catalyst poisoning and environmental emissions; (d) ashless antiwear or "lubricity" additives for fuels, including gasoline, diesel and jet fuel; (e) vapor phase applications of this technology to high temperature gaseous systems or to fuel injector wear problems associated with the use of natural gas engines; and (f) the use of the concept of tribopolymerization as an enabling technology in the development of new engines and new automotive propulsion systems.

DISCLAIMER

Introduction

In research conducted in the Tribology Laboratory at Virginia Polytechnic Institute and State University, it has been demonstrated that the principle of tribopolymerization developed by Furey and Kajdas can be used as a novel and effective approach for lubrication of metals and ceramics, in fuels as well as conventional lubricants, and in both liquid and vapor phase applications. The concept has potential in addressing several issues relating to advanced automotive technology -- issues which connect with or are related to effectiveness in reducing wear, efficiency, energy savings, environmental benefits, and enabling technology.

The major purpose of this paper is twofold: (a) to describe potential applications of the concept of tribopolymerization, with emphasis on design, manufacture, testing, operation, and performance of systems which relate or could relate to the development of advanced automotive technologies, and (b) to present several examples of results obtained by applying this concept to diverse systems, including steel and ceramic tribological systems.

Tribopolymerization

Tribology -- derived from the Greek "τριβω" (to rub) -- is the study of friction, wear, and lubrication [1]. By tribopolymerization, we mean the planned, intentional, and continuous formation of protective polymeric films directly on tribological surfaces by the use of minor concentrations of selected monomers capable of forming polymer films "in situ" either by polycondensation or addition polymerization[2-6]. The approach involves the design of molecules which will form thin, deposited polymeric surface films in critical regions of lubrication--thus reducing contact and wear.

An oversimplified view of the process is shown in Fig. 1.

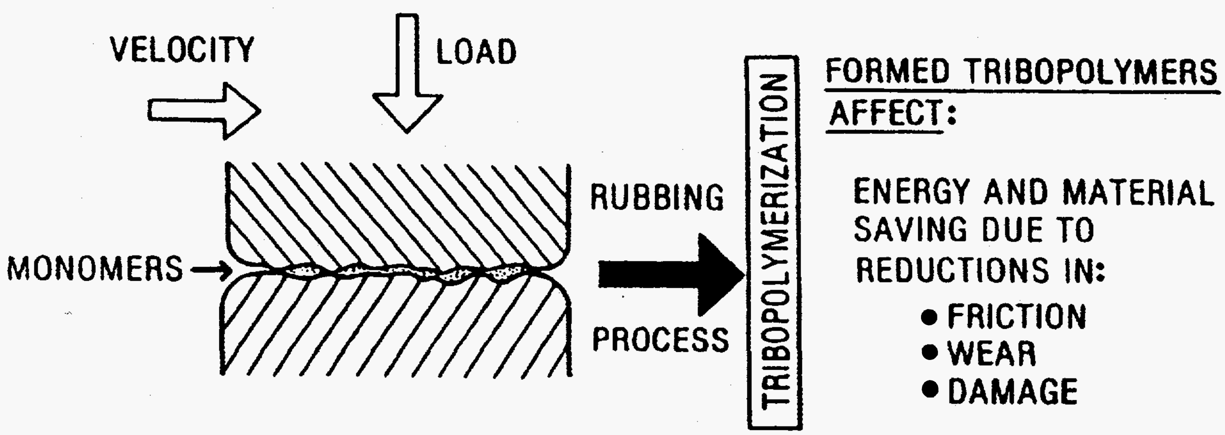

Fig. 1. **Tribopolymerization as a Mechanism of Boundary Lubrication**

Although the detailed mechanisms of surface film formation are not yet fully understood, the central and unique feature of tribopolymerization is that it is primarily a process of controlled deposition on a high surface temperatures generated by friction, high contact pressures, and exoelectron emission from rubbing surfaces. The protective polymeric films formed are extremely thin and generally invisible. The films formed reduce adhesion and wear in a continuous formation/removal/replenishment process. It is important to note that we do not coat mechanical elements with polymers prior to rubbing contact; the coatings would wear off and no longer be effective. Neither do we add polymers to a fluid carrier. By the concept of tribopolymerization, we need to use the embryonic monomeric molecules in a carrier fluid to form the protective polymeric surface films continuously only where needed -- in critical regions of boundary lubrication -- and not on all parts of an engine or system. It is a technique of molecular design in which three main aspects are important, i.e., (a) the structure and surface orientation of monomeric molecules prior to polymerization, (b) the process of tribopolymerization, and (c) the properties of the films formed (e.g., adhesion, thermal and mechanical stability, durability).

Potential Applications of Tribopolymerization Technology

- New ashless lubricants for existing and future automotive engines to reduce exhaust catalyst poisoning and environmental emissions.
- Lubrication of ceramic engines (e.g., low heat rejection diesel engines) or ceramic components (e.g., turbochargers, cam followers, valve guides, cylinder liners, seals, and bearings).
- Ashless antiwear or "lubricity" additives for fuels, including gasoline (2-stroke engines), diesel (e.g., to reduce fuel injector wear occurring with low sulfur fuels), jet fuel (e.g., to minimize fuel pump wear), and CNG/LNG engines. Reduced fuel injector wear problems in natural gas engines
- Vapor phase applications of this technology for high temperature gaseous systems.
- Machining and cutting applications using minimal thin films to reduce friction and ceramic tool wear, especially on difficult metals, and minimize lubricant waste and disposal.
- The use of the concept of tribopolymerization as the enabling technology in the development of new components, engines and new automotive propulsion systems.

Examples of some of these applications follow.

Boundary Lubrication of High Contact Stress Steel Systems

A large number of monomers have been investigated as tribopolymer-forming compounds in our research on lubrication under boundary conditions. An outstanding example of the application of this concept to a real problem was demonstrated by the striking effectiveness of partial (e.g., mono-) esters made by reacting long-chain C_{36} dimer acids with glycols (e.g., ethylene glycol). These compounds were postulated to act by the formation of polyester films as follows:

$$\underset{\text{monoester}}{n\,HOOC\text{-}RCOO\text{-}C_2H_4OH} \xrightarrow{\text{Rubbing Surfaces}} \underset{\text{polyester}}{HO\text{-}[OC\text{-}R\text{-}COO\text{-}C_2H_4O]_n\text{-}H} + \underset{\text{water}}{H_2O}$$

The effectiveness of the above monoester and related potential polymer formers in reducing tribological damage was first demonstrated by the results of tests in the Ryder Gear Machine -- a sophisticated test device designed to measure the ability of a lubricant to prevent gear scuffing. Some examples of these results are shown in Table 1.

Table 1. **Effect of the C_{36} dimer acid/ethylene glycol monoester on the antiscuff properties of fuels and lubricants**

Base Fluid	Ryder Gear Scuff Rating (N/cm) on: Base Fluid	Base + 0.1% Monoester
Jet Fuel	700	2600
Turbo Fuel	900	3700
JP-4	350	5200
Xylene	900	6100
Mineral Oil (neutral, 43 SUS/210F)	2100	4400
Synthetic Oil (C_8-C_{10} Oxo Adipate)	3000	4600

For the four fuel-type low viscosity fluids shown (i.e., jet fuel, turbo fuel, JP-4, and xylene), the increase in scuff rating brought about by the addition of only 0.1% of the monoester ranged from 1900 to 5200 N/cm corresponding to roughly a four to fourteen-fold increase. The results are extraordinary; in fact, fuels containing the monester have greater load-carrying capacity than several mineral and synthetic aviation oils [2,3]. And fuel pump wear in field tests with jet fuels was drastically reduced.

Tests of the "in situ" polymer film approach to boundary lubrication under severe conditions were also carried out using a V-8 automotive engine. Wear was determined continuously during a test by using a normal engine equipped with radioactive valve lifters -- a technique developed by Furey. The results of tests using mixtures as well as single compounds supported the concept of tribopolymerization as an effective approach to controlling valve train wear -- one of the most critical regions of lubrication in an automotive engine[2,3].

As an example, it can be seen by the data in Table 2 that the addition of 1% of the C_{36} dimer acid/ethylene glycol monoester to a mineral oil base reduced the rate of wear by over 90%. This is roughly equal to the outstanding effect of zinc dialkyldithiophosphate additives which have been used in automotive engine lubricants since the early 1950's to control valve train wear.

Table 2. **Effect of the C_{36} dimer acid/ethylene glycol monoester on valve train wear**

Compound in Paraffinic Mineral Oil	Relative Valve Lifter Wear Rate
None	100
1% C_{36} Dimer Acid/Ethylene Glycol Monoester	8
1% Zinc Di(C_6) Alkyl Dithiophosphate	12

Other evidence in support of the "in situ" polymer former mechanism was also obtained in this earlier study, including the results of mechanism studies in a dynamic sliding system with radioactivity-labeled compounds[2,3].

Fundamental studies of tribopolymerization as a mechanism of boundary lubrication for metals (e.g., steel) as well as ceramics were carried out under research grants from the National Science Foundation[5-12]. The tribological tests were carried out using a ball-on-flat type contact geometry, i.e., in a pin-on-disk test device. The test conditions used are designed to emphasize boundary lubrication under severe conditions. As an indication of the severity, an applied load of only 20N corresponds to a calculated mean Hertz pressure of 2.6 GPa for the alumina system used in our research. The calculated elastic contact pressure on the highly loaded cam nose of a typical V-8 automotive engine valve train is roughly 1 GPa.

The C_{36} dimer acid/ethylene glycol monoester already discussed as an effective additive for jet fuel "lubricity" as well as in reducing valve train wear was also examined in pin-on-disk tests using steel-on-steel (AISI 52100 steel balls on 1045 polished steel disks). The compound was very effective in reducing wear at different levels of applied load. At 10 N load, the addition of 1% of monoester to hexadecane reduced disk and ball wear by over 80% and 50%, respectively. In tests under partial oil starvation conditions and the same load (10N), the effects were even more dramatic. Under these conditions, the monoester reduced disk wear by over 95%. FTIRM surface analysis of the worn specimens showed evidence of both metallic soap formation and polymerization [5]. Some examples of results obtained with ceramic systems are discussed in the next sections.

Tribopolymerization and Ceramic Lubrication

For tribological applications, ceramics offer several advantages over conventional materials. Ceramics are thermally stable to much higher temperatures, and are relatively inert and corrosion resistant. Ceramics are hard, and thus more resistant to abrasive or erosive wear. And some ceramics are lighter in weight than alloy steels commonly used in engines and machines. Examples of tribological applications of ceramic materials include ceramic engines for higher temperature operation and greater thermodynamic efficiency; advanced propulsion systems; turbomachinery and gas turbines; aerospace bearings; automotive engine components; cutting and machining tools for difficult alloys; biomedical products (e.g., artificial joints); ceramic heads for magnetic recording; and any tribological system operating under high temperature, abrasive, or corrosive conditions. However, conventional approaches to the lubrication of ceramics are limited (e.g., surface coatings or treatments) or often ineffective [7]; and commonly-used lubricants and additives designed for steel systems generally do not work.

In an initial exploratory study by Furey and Kajdas at Virginia Tech, it was clearly demonstrated that the principle of tribopolymerization can be used as a novel and effective approach to designing specific molecular structures for the lubrication of ceramic materials. In high contact stress (pin-on-disk) sliding tests with a variety of ceramics, it was found that the addition to a carrier fluid lubricant of minor amounts of particular compounds reduced wear by 40 to 80%. A reduction of wear by 80% amounts to an increase in life of a ceramic element by a factor of five. In addition, friction reductions up to 35-40% were obtained. In this initial study, several ceramic systems were investigated, including alumina-on-alumina (Al_2O_3), zirconia-on-zirconia (ZrO_2),silicon nitride-on-silicon nitride (Si_3N_4), and sapphire-on-sapphire (Al_2O_3) [7-12]. Some addition-type monomers were found to reduce ceramic wear by over 80% at concentrations as low as 0.02%.

Vapor Phase Lubrication

Studies have also been carried out on the application of the tribopolymerization concept to vapor phase lubrication -- an area of increasing interest, particularly for high temperature boundary lubrication (e.g., of engines and propulsion systems). Using a modified pin-on-disk machine, the effects of several addition-type monomers on wear were investigated. The liquid compounds were heated, vaporized and delivered to an enclosed alumina-on-alumina contact region by a stream of dry nitrogen gas. The vapor concentrations were low, e.g., 0.00002 to 0.005 gmolℓ^{-1}.

Dramatic reductions in wear occurred, particularly for those vapors delivered at higher temperatures. Alumina ball wear reductions of up to 99% were observed. And at elevated bulk temperatures (145°C), the monomers in the vapor phase reduced friction coefficients by as much as 50%. An example of the effect of one monomer, lauryl methacrylate, on alumina wear is shown in Fig. 2. It can be seen that at a bulk temperature of 145°C, increasing the vapor delivery temperature reduces wear by as much as 94%. Greater reductions (e.g., 99%) were observed with other monomers at higher temperatures (e.g., 165°C)[11]. FTIRM analysis of the worn surfaces suggests that the film-forming mechanism is complex -- involving not only a strong surface or bonding reaction with alumina but also tribopolymerization.

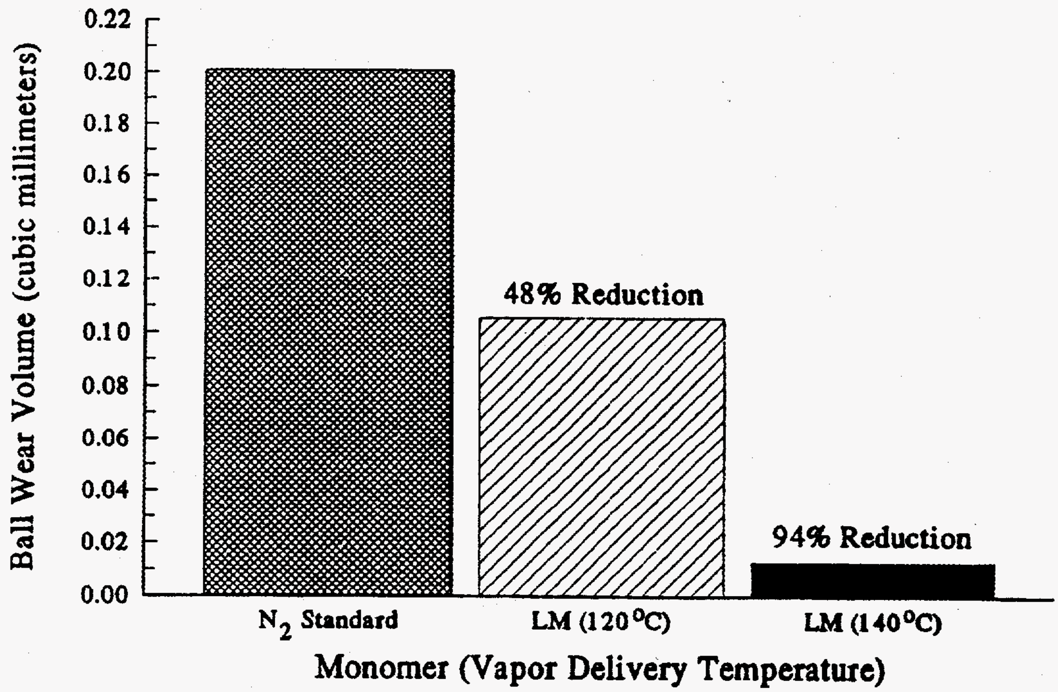

Fig. 2. **Effect of Lauryl Methacrylate Vapor on Ceramic Wear Using Nitrogen as the Carrier Gas (145°C Bulk Temperature) [11]**

The practical significance of this work is that it demonstrates an effective approach to boundary lubrication in the vapor phase in the absence of any special prior treatment or added catalytic films to promote a reaction. Suitable carrier gases include air, nitrogen, exhaust gases, etc. The method is also applicable to the boundary lubrication of metals (e.g., steel)

Recognition by the U.S. Department of Energy/ Energy-Related Inventions Program

Our discovery that the principle of tribopolymerization is a useful and often strikingly effective approach to the lubrication of ceramics as well as metals was selected as one of 12 out of 600 proposals in the U.S. Governments DOE Energy-Related Inventions Program. An extract from the Executive Summary of the NIST Evaluation of this invention states:

"...The invention holds promise of being a better way to lubricate adiabatic engines than current techniques. Thus it could become an enabling technology for ceramic internal combustion engines."

In addition, a market assessment study was carried out by the U.S. National Center for Appropriate Technology. Some comments from the Executive Summary of the report follow below.

"The subject invention is an innovative process for lubricating ceramic surfaces. Good market potential exists if it can lubricate ceramic-metal interfaces at a reasonable cost...

The market potential is greatest in the engines, aerospace, machine tools, and the turbomachinery segments...

Industrial involvement and collaboration with various companies (e.g., engine and engine component manufacturers, lubricant and additive suppliers) to field-test and eventually market the new lubricants and products that evolve from this research, is crucial."

Under a grant from the Department of Energy under this program, studies have been carried out to demonstrate the merit of the concept of tribopolymerization under more severe conditions of load, speed, and frictional heat generation. A high load/high speed pin-on-disk machine was developed for this research; loads as high as 16ON and sliding speeds of 1 m/s are possible -- a 32-fold increase in frictional heat generation. Using this machine, new classes of monomers designed for higher temperature applications were developed; these were found to be extremely effective in reducing wear at high loads and seeds. Results of this more recent research will be presented in the future.

Tribopolymerization for Machining and Cutting

Since ceramic tools are widely used in the machining and cutting of metals and other materials, an exploratory study of ceramic tool wear and lubrication was carried out using the tribopolymerization technique.

Tests were conducted in the Industrial Engineering Systems Laboratory using an instrumented 10hp Mazark lathe. The workpiece was a six-inch diameter solid cylinder of AISI 4340 alloy steel; the length of the cylinder was 36 inches. The Kennametal ceramic tools used consisted of vitrified alumina-titanium carbide inserts (70% Al_2O_3 + 30% TiC). A micro lubrication system was devised -- one using a very low, controlled flow rate of lubricant through a nylon flow gun brush. This method continuously applied an extremely thin, almost invisible film of fluid just prior to the cutting region. Strain gages are used to measure tool forces in three directions.

The results of the initial study were quite interesting. First of all, reductions in friction of 30-40% over dry cutting were observed; this results in energy savings. Secondly, several of the monomers tested reduced tool crater and tool tip wear when used as additives at 1% concentrations in hexadecane. Average reductions in tool crater wear ranged from 15 to 40% while tool tip wear was reduced by 30 to 60% over dry cutting. In experiments using a very thin film of a pure liquid monomer, friction was reduced by 40%, tool crater wear by 30%, and tool tip wear by 85%. These results are significant not because ceramic tools are costly (many are not) but because the down-time involved in replacing a worn tool or defective part means lost money. The study also demonstrated that this chemical, tribopolymerization approach to "minimalist lubrication" could lead to improved surface finish over dry cutting although this was not always observed. Since the method relies on specific chemistry at the tool/workpiece interface -- a region of extremely high frictional energy and surface temperatures -- rather than bulk cooling effects, it is possible to carry out machining and cutting operations with much less cutting fluid

Replacement of conventional cooling lubricant fluids with micro quantities of tribopolymer-forming compounds could reduce waste product streams, air borne mist hazards, and contamination on the work parts. Currently in some machining operations, the costs relating to coolants and lubricants exceed the combined costs of tooling, labor, energy and capital. Operating cost reductions are achieved by eliminating the purchase of large volumes of coolants and lubricants, their process treatments, and final disposal costs. Capital cost reduction is achieved by extending the life of existing machine tools with micro lubrication using these monomers.

Conclusions

1. The concept of tribopolymerization as a novel and effective mechanism of boundary lubrication and wear-reduction was described. The method, developed by Furey and Kajdas, is a process of molecular design. Tribopolymerization is defined as the planned and continuous formation of protective polymeric films "in situ" on rubbing surfaces by the use of minor concentrations of compounds selected or synthesized on the basis of this concept.

2. The method has been shown to be extremely effective with metals (e.g., steel) as well as a variety of ceramic materials in high contact stress tribological systems and in both liquid and vapor phase experiments. Several examples were given. These included striking effects observed in gear scuffing tests using fuel and lubricant carrier fluids, automotive engine valve train wear, boundary lubrication of steel and ceramics, and machining/cutting processes.

3. Advantages of tribopolymerization as a mechanism of reducing wear and friction under boundary lubrication conditions were discussed. The compounds are ashless, contain no phosphorus or sulfur, and are generally biodegradable. Thus they offer advantages as ashless antiwear additives, fewer problems with catalytic exhaust gas converters, and as fuel antiwear additives. A wide range of possible applications of this technology was also presented.

4. Fundamental research and further development on tribopolymerization in the Tribology Laboratory at Virginia Tech has been supported by grants from the U.S. National Science Foundation, the Department of Energy, Virginia's Center for Innovative Technology, and Triad Investors Corporation. The approach was also recognized by the U.S. Governments Energy - Related Inventions Program. We gratefully acknowledge their support.

5. Surface analytical studies using Fourier Transform Infrared Microspectrometry show that the film-forming process involves a combination of chemical bonding to the substrate coupled with polymerization. New compounds capable of reducing wear at high loads, speeds, and rates of frictional heat generation have been developed based on this concept.

6. Patents based on this technology, e.g., [13], have issued and others are pending. Arrangements for licensing, field testing and evaluation, and marketing can be made by contacting Triad Investors Corporation, 300 East Joppa Road, Baltimore, Maryland 21286 under an agreement made with Virginia Tech Intellectual Properties and the Office of Sponsored Research at Virginia Polytechnic Institute and State University.

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