Tech Beat

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Empirical testing of a universal law for surface wear

Wear is defined as the gradual loss of material from a solid surface due to its interaction with a second contacting surface. For example, abrasive wear occurs particularly when tall sharp asperities from a hard surface produce gouges on a softer surface.

STLE member Dr. Matthew Siniawski, assistant professor of mechanical engineering at Loyola Marymount University in Los Angeles, says, "Surface wear is a major problem in reducing the lifetime of machinery. Efforts to better predict wear can provide a number of benefits, including greater energy conservation and improved productivity."

The challenge in finding a universal wear law that works is due to the complexity of the rate of removal of material from a surface over time.

Development of theoretical models to characterize wear has been a major objective because it can reduce the amount of testing needed to verify the efficacy of anti-wear coatings and potentially allow for smaller margins of safety in the design of machinery. A number of models have been proposed to explain surface wear.

Siniawski comments, "Most of these models are good building blocks and provide a greater understanding of wear. However, they are only effective for specific materials under specific conditions and cannot be applied to other systems."

The challenge in finding a universal wear law that works is due to the complexity of the rate of removal of material from a surface over time. Siniawski believes that the impact of changes in the composition of both interacting surfaces over time at the microscale has a significant impact on the surface wear.

Equation (1) developed in 1998 by Stephen Harris and coworkers provided a good prediction for the wear rate of steel sliding against diamond-like-carbon (DLC) coatings.[1] Siniawski and colleagues tested this relationship by sliding 52100 steel ball bearings against coupons coated with boron carbide (B_4C) and DLC in pin-on-disk experiments. He says, "We tested the ball bearing over 10^5 cycles and obtained experimental validation for equation (1). This equation is shown below.

$$\mathbf{A(n) = V(n)/d = A_1 n^B} \qquad (1)$$

A(n) represents the wear rate averaged over the first n cycles. V(n) is the volume of steel removed from the ball during the first n cycles of the test and d is the distance of the steel ball traveled over the disk. A_1 represents the wear rate of the first cycle.

The "B" term is a measure of the cycle or time dependency of the wear rate. Siniawski indicates that "B" can range from -1 to 0. The former would occur if all of the system's ability to generate wear is lost after the first cycle. If "B" is 0, then the wear rate would be constant during the process. For the initial experiments of the 52100 steel ball on the DLC and B_4C coatings, "B" was found to be -0.8. Siniawski explains, "There is an indirect relationship between the wear rate and "B." The wear rate cannot fall faster than inversely with the number of cycles completed."

Experimental validation

Siniawski conducted work to determine if equation (1) can be used to predict the surface wear of a system, given A_1 and "B." An example of this work, carried out by Siniawski using 52100 steel, is shown in Figure 1. Siniawski says, "We looked at the wear rate of 52100 steel as a function of the cycles using boron carbide coatings of varying surface roughness (R_a). Equation (1) does a very good job of predicting actual performance over a wide range of boron carbide surface roughness."

The graph on the bottom left in Figure 1 shows the decline in the surface roughness of the steel, as the number of cycles increases to 1,000. Equation (1) shows good predictability of abrasive wear, as seen in the graph on the bottom right of Figure 1.

Scanning electron microscopy (SEM) images of the boron carbide coating are also shown for the unworn (*on the left*) and the worn (*on the right*) surfaces. The worn boron carbide coating surface image was taken after 500 cycles.

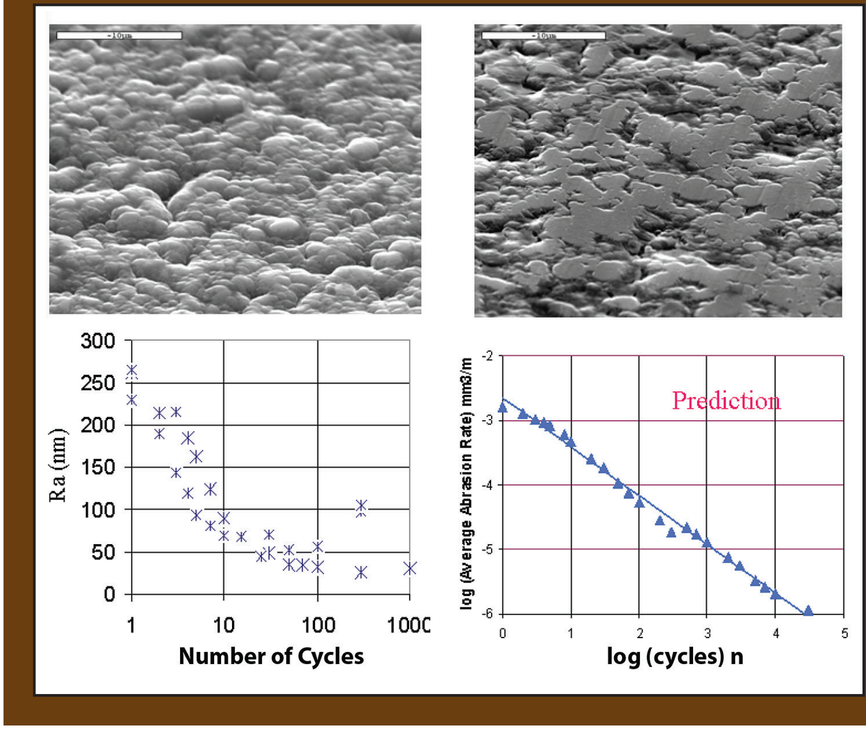
Boron carbide is a very abrasive coating while steel is a semisoft surface. Siniawski says, "We found that 52100 steel chemo-mechanically polishes the boron carbide surface at the same time that the much more abrasive boron carbide is mechanically polishing the steel."

Siniawski points out that the tall sharp asperities in any surface are much easier to dull during the process of abrasive wear. He adds, "The really tall sharp asperities wear down quickly, while the remaining hidden asperities on a surface wear down later. These asperities are shorter and tend to be protected by the taller asperities. In addition, those asperities that are duller take a lot longer to wear down."

All of the previous work described was carried out without any lubricant. Siniawski evaluated the 52100 steel boron carbide system with a neat paraffinic oil exhibiting a viscosity of 20 cSt at 40C. He says, "The use of a lubricant lowered the wear rate, and the wear of the system can still be accurately predicted with equation (1)."

Siniawski found that this decrease in the wear rate was only partly attributed to the use of a lubricant. He adds, "The pretty severe boundary lubricant conditions make it difficult for a neat base oil to be more of a factor in reducing wear." Siniawski plans in future work to evaluate other lubricants that are formulated with anti-wear and extreme pressure additives to see if equation (1) can be used to predict surface wear of more systems with more complex lubricants.

Figure 1.



(Courtesy of Loyola Marymount University)

Scanning electron microscopy (SEM) images of boron coatings are shown on the top. The figure on the top left is the unworn coating and the figure on the top right is the worn coating after sliding against 52100 steel for 500 cycles. The graph on the bottom left shows the decline in the surface roughness of steel, as the number of cycles increases to 1,000. Good predictability of equation (1) is seen on the bottom right graph.

Additional testing also was carried out with vegetable oil-based lubricants that are chemically different than paraffinic base oils. Equation (1) was also found to be accurate in predicting the surface wear of steel with vegetable oil-based lubricants.

Siniawski next examined literature data and evaluated empirical work described in 17 publications that cover systems with a wide range of materials and contact conditions. In each case, equation (1) provides a good wear predictability for the results. He says, "We found the root-mean-square (RMS) deviation between the data and equation (1) to vary at the maximum by 10%. In most cases, the deviation was less than 5%."

Equation (1) shows promise to be a universal law for surface wear and could possibly be one of the Holy Grails of tribology. Future work will involve learning more about how proper material selection, surface roughness and other parameters influence both A_1 and "B."

Siniawski, says, "If that can be achieved, equation (1) could potentially be used to predict the surface wear of any system. Another approach would be to develop a concise empirical database of values of A_1

CONTINUED ON PAGE 14

CONTINUED FROM PAGE 13

and "B" that can be used by tribologists to predict wear for a specific system. Use of equation (1) could significantly reduce the amount of experimental testing needed to determine wear rates for specific machinery systems prior to use."

Details about equation (1) including references covering its origin are included in a recently published paper.[2] Additional information also can be obtained by contacting Siniawski at **msiniawski@lmu.edu**.

References

1. Harris, S., Weiner, A., Olk, C., Grischke, M. (1998), "Effects of Nanoscale Morphology on the Abrasion of Steel by Diamond-like Carbon," *Wear*, **219**, pp. 98-104.

2. Siniawski, M., Harris, S. and Wang, Q. (2007), "A Universal Wear Law for Abrasion," *Wear*, **262**, pp. 883–888.

New synthetic basestocks from a renewable source

The increasing requirements placed on lubricants to provide a high level of performance over increasing long and demanding operating time frames has led the industry to utilize more and more products derived from synthetic basestocks. Lubricants are marketed based on such basestocks as polyalphaolefins (PAOs), esters (di and polyol), polyalkylene glycols (PAGs) and phosphate esters.

> **'Instead of conducting chemical transformations on a high molecular weight natural raw material, we take a renewably sourced small molecule and build it up in a polycondensation reaction to form a polyether diol.'**

Many of these basestocks have been made in the past by raw materials derived from petroleum oil (petrochemicals). With the increasing trend toward using environmentally friendly raw materials, the chemical industry has been looking to use renewable sources such as carbohydrates, proteins and lipids.

One chemical intermediate that has been used in the manufacture of polyester fibers is 1,3-propanediol, also known as PDO. This intermediate has been produced in the past from propylene or via a hydroformylation process from ethylene oxide.

Recently, DuPont and Tate & Lyle have commercialized an alternative process for manufacturing PDO from corn-derived glucose through a fermentation process. Glucose is converted into PDO through the assistance of a metabolically engineered version of E. *coli*. Commercial production of Bio-PDO™ from glucose started up late in 2006.

Polyether diols

DuPont is now in the process of commercializing Cerenol™, a new family of renewably resourced, high-performance polyols (polyether diols). Certain grades of Cerenol will be a type of synthetic basestock for functional fluids. The polyether diols are prepared by polymerization of biobased PDO. Molecular weights for these polymers range from 500 to 3,000.

Ray Miller, new venture manager for biobased materials for DuPont, says, "We have taken a different approach in the development of a biobased lubricant basestock. Instead of conducting chemical transformations on a high molecular weight natural raw material, we take a renewably sourced small molecule and build it up in a polycondensation reaction to form a polyether diol."

One of the first objectives was to ensure that these renewably sourced polyether diols exhibited a very low toxicity profile. Testing carried out indicates that the polyether diols are not skin and eye irritants, and they also are not skin sensitizers. A very low acute oral mammalian toxicity (LD50 > 2000 mg/kg) also was verified.

The polyether diols represent a family of new products that contain both homopolymers and copolymers. Miller says, "We can tailor the polyether diol to meet specific applications and customer requirements.” For example, the terminal hydroxyl groups present on these polymers can be converted into esters through treatment with organic acids.

Biodegradability testing is in the process of being carried out on the polyether diols. Hari Sunkara, research associate for DuPont, says, “Biodegradability depends on the type of product and is determined by parameters such as molecular weight and water solubility. Those polyether diols that exhibit low molecular weights and are soluble in water are mainly biodegradable.”

The polyether diols useful in lubricant applications are not all homopolymers manufactured from PDO. Sunkara says, “We found that addition of ethylene glycol as a co-monomer in the polymerization leads to improved low-temperature properties for polymers with molecular weights ranging from 500 to 1,500.”

The pour point of polytrimethylene ether glycol (homopolymer prepared from PDO) is -24 C. Inclusion of ethylene glycol will enable the pour point to drop to between -40 C and -60 C.

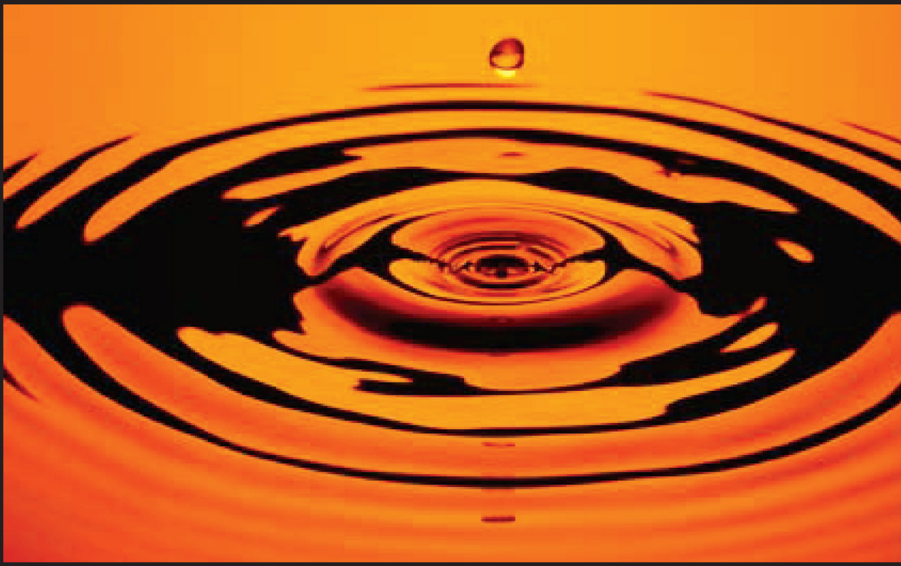
Polytrimethylene ether glycol exhibits superior thermal and oxidative stability properties. A homopolymer with a molecular weight of 500 displays a flash point of 235 C.

The polymer was evaluated for oxidative stability by the ASTM D2272 procedure, which is known as the RPVOT (Rotating Pressure Vessel Oxidation Test). A known antioxidant (phenothiazine) was added at a 1% treat rate and the polyether diol evaluated at 150 C. Failure was not seen until 415 minutes. Sunkara says, “A conventional mineral oil will fail at between 80 and 90 minutes under the same test conditions.”

He adds, “Polyether diols do not contain tertiary carbons in the backbone, which enables them to exhibit superior oxidative stability as compared to other polyethers. This property is unexpected because it was anticipated that the linear nature of polyether diols combined with the greater number of ether linkages would lead to inferior oxidative-stability properties.”

Polyether diol homopolymers and copolymers are being evaluated as synthetic lubricant basestocks in a number of applications, including dielectric fluids, gear oils, heat transfer fluids and hydraulic fluids. Miller says, “Our objective is to determine in which applications polyether diols display superior characteristics.”

Figure 2.



(Courtesy of DuPont)

A new family of renewably resourced, high-performance polyols (polyether diols) has been developed that can be used as a synthetic basestock for functional fluids.

Initial work as a basestock in heat transfer fluids has shown promise. Sunkara says, “Polyether diols exhibit good thermal conductivity values that enable them to be suitable for use in heat transfer fluids.”

Polyether diol homopolymers also have been evaluated as dielectric fluids. Blending with an ester or a vegetable oil is preferred to provide dielectric breakdown voltages greater than 30 kv.

‘Polyether diols exhibit good thermal conductivity values that enable them to be suitable for use in heat transfer fluids.’

Miller says, “Evaluation of polyether diols in lubricant applications will be completed in 2008. At that time we will be able to provide additional information about their performance characteristics and how best they can be used as synthetic basestocks. We see polyether diols as very attractive for the lubricant market because they are prepared from renewably sourced materials and can meet the requirements of high-performance functional fluids.”

DuPont is in the process of commercializing this new line of renewably sourced, high-performance polyether diols. Additional information can be requested at **cerenol@usa.dupont.com**.

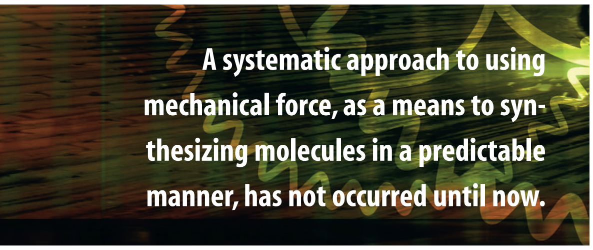
CONTINUED ON PAGE 16

CONTINUED FROM PAGE 15

Mechanochemistry: A new approach to synthesize molecules

As a chemist who has worked on synthesizing specific molecules, I have often been frustrated when a specific reaction approach did not work. Lessons learned from experimentation have proven to be useful in finally developing the right strategy to prompt the reactant molecules to act in what I would consider the "right way."

Often enough, I have wanted to stick my hand in the reaction flask and literally "beat" on the molecules to force them to react in a manner that I wanted them to do. This frustration from my past is brought up because most techniques available to convert one molecule to another have entailed the use of either heat or light to enable the reaction to succeed.



A systematic approach to using mechanical force, as a means to synthesizing molecules in a predictable manner, has not occurred until now.

In lubrication, some additives will not function unless they reach a specific temperature. An example of this, discussed in the September TLT, which featured a special report on extreme pressure (EP) additives, is the need for three of the specific EP additive classes to become activated when the temperature of the lubricant application reaches a specific point. EP additives will then form metal salt barriers that reduce friction and wear.[1]

If a molecule could be activated through a mechanical process, then there may be an opportunity to develop new technologies that could be incorporated into metal surfaces for use when the force or pressure reaches a specific level. Once the molecule is activated mechanically, it would then be able to exhibit extreme pressure characteristics.

The use of force on molecular systems has led to the fracturing of molecules in a random manner in the past. A systematic approach to using mechanical force, as a means to synthesizing molecules in a predictable manner, has not occurred until now.

Use of mechanophores

Jeffrey Moore, William H. and Janet Lycan, professor of chemistry at the University of Illinois at Urbana-Champaign, led a research team that has developed a process for driving chemical reactions through the use of mechanical force. He says, "We consider this type of reaction to be mechanochemistry. The key to mechanically inducing reactions is to activate the molecule in a predictable manner. This approach can be accomplished through the use of a specific molecular unit activated by mechanical force, which is known as a mechanophore."

The mechanophore chosen by the research team is benzocyclobutene (BCB). Moore adds, "BCB contains a four-member ring that is sterically strained and susceptible to a systematic bond breakage under stress."

BCB was incorporated into the center of a polyethylene glycol (PEG) polymer with molecular weights ranging from 4 to 60 kDa. The reaction was monitored by having the activated BCB react with a maleimide to form a compound that could be detected by gel permeation chromatography (GPC) using ultraviolet light.

The mechanical force was provided by ultrasound at a frequency of 20 kHz. The researchers detected a reaction at a temperature between 6 C and 9 C, too low for the process to occur thermally. Moore says, "The real reason we chose this system was that the chemistry for the thermal reaction is well known. We deliberately chose conditions under which heat could not induce the reaction."

The reaction is known as an electrocyclic process in which one bond in the strained, four-member ring is broken. This enables the ring to be opened in a specific manner. Organic chemists know that the Woodward-Hoffmann rules have been developed to determine how the ring should open in the presence of heat and light.

Two isomers (cis and trans) of the BCB-based polymer were evaluated. The research team found that mechanical stress forced the ring openings of both isomers to generate the same intermediate isomer. This finding was consistent with a computational analysis carried out using the COGEF (COnstrained Geometries simulate External Force) method.

In fact, the cis isomer produces a different intermediate isomer than is found with the use of heat. In the case of the trans isomer, the same intermediate isomer is detected with both the use of mechanical energy and with heat.

Mechanical force mechanism

Moore indicates the mechanism for the use of mechanical force is not known. He says, "We believe that the acoustic field generated by the ultrasound creates cavities in the order of microns (up to 100 microns). These cavities form slowly but collapse rapidly. During the collapse, solvent molecules violently rush past the polymer chains toward the collapsing cavities to fill the voids. The resulting stress on the polymer chain leads to the bond breakage in the mechanophore."

Moore indicates that the polymer chain is in a velocity gradient. Most of the stress is felt in the middle of the chain, which is the location for the mechanophore. One end of the chain is sucked into the collapsing cavity, while the other end is a drag on the entire chain.

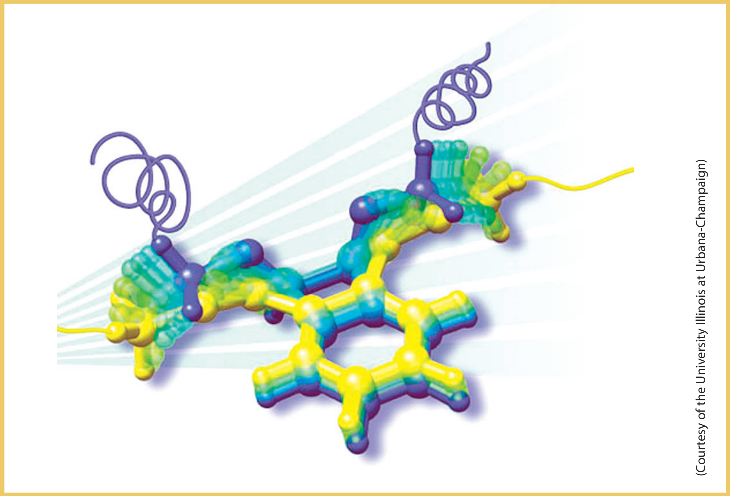
Figure 3 is an overlay of three images showing how mechanical force causes the reaction to occur. The colored image represents the BCB group, while the two strains represent the polymer chain. The blue colored image is how BCB looks at the beginning of the reaction, while the yellow colored structure shows the end of the reaction.

Moore sees a number of applications for mechanochemistry. He says, "We envision that a color-generating mechanophore could be produced in a mechanically induced reaction by, for example, scratching a polymer film. The mechanophore could act as a probe to assist with mapping out stress fields associated with the polymer film."

A second application envisioned by Moore is to use mechanophores as a catalyst that could, for example, release a proton under stress to drive a specific process. This feature combined with the color-generating mechanophore could lead to the use of a color-generating sensor that is triggered by force to turn on and catalyze a reaction.

If the right type of mechanophore can be found, then it is not too difficult to envision lubricant additives placed on a surface that can be mechanically activated by this type of technology. Further information can be found in a recently published paper.[2] <<

Figure 3.



(Courtesy of the University Illinois at Urbana-Champaign)

The BCB mechanophore used in the process is placed in the middle of a polymer chain (*represented by the attached strands*). The blue image of the mechanophore represents the start of the reaction. The yellow image represents the end of the reaction. Ultrasound is used to generate cavities that collapse rapidly as solvent molecules (*shown in the green gradient*) rush past the mechanophore.

> **'The key to mechanically inducing reactions is to activate the molecule in a predictable manner. This approach can be accomplished through the use of a specific molecular unit activated by mechanical force which is known as a mechanophore.'**

References

1. Canter, N. (2007), "Trends in Extreme Pressure Additives," *Tribology and Lubrication Technology*, **63** (9), pp. 10–18.

2. Hickenboth, C., Moore, J., White, S., Sottos, N., Baudry, J. and Wilson, S. (2007), "Biasing Reaction Pathways with Mechanical Force," *Nature*, **446** (7134), pp. 423–427.

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