



Nanoparticle-Based Lubrication Systems

Mustafa Akbulut*

Artie McFerrin Department of Chemical Engineering, Materials Science and Engineering Program, Texas A&M University, 230 Jack E. Brown Engineering Building, 3122 TAMU, College Station, TX 77843-3122, USA

Abstract

With the advent of nanotechnology, research into lubricants and lubricant additives has experienced a paradigm shift. Instead of traditional materials, new nanomaterials and nanoparticles have been recently under investigation as lubricants or lubricant additives because of their unusual properties. Now, there are numerous different types of nanomaterials with potentially interesting friction and wear properties described in the literature. With increasing amount of possibilities, the key question is: what types of nanoparticles act as better lubricants and why? This article will discuss relevant issues to this topic.

For any machine to operate smoothly, some energy must be provided for the sole purpose of overcoming friction. Minimizing energy lost through friction increases the efficiency of machines. Recent studies have indicated that advances in tribology could lead to savings of approximately 11% of total annual energy loss in three major areas: power generation, transportation, and industrial processes [1]. Therefore, in the context of energy efficiency, the significance of reducing friction cannot be overemphasized. This is especially true as oil reserves continue to dwindle and energy costs are rising relentlessly.

In addition, friction and wear are two major reasons vital engineering components in various systems fail, such as gears, pin-joints, pistons, bearings, camshafts, pumps, compressors, and turbines. The cost of equipment, installation, and repair related to frictional deficiencies, wear, and damage places an enormous burden on any national economy.

Furthermore, lubricant technologies have not kept up with advances in the manufacturing, energy, and defense industries. In fact, tribological and mechanical limitations have been shown to be the critical factors hindering the transition from prototype to product in many high-tech applications. Therefore, as existing lubricants reach their performance limits, one of the major scientific challenges for the 21st century is to develop new lubricants that fulfill the emerging requirements in diverse strategic fields, from energy to transportation or manufacturing, for use under increasingly more stringent conditions.

This editorial will discuss nanoparticle-based approaches in this quest for the design of novel and superior lubricants. In this context, this article will specifically seek answers to the following key question: what are the important characteristics of nanoparticle-based lubrication systems that provide superior lubrication properties?

In the light of current literature [2-18] size, shape, nanostructure, surface functionalization, and concentration of nanoparticles have emerged as the most critical parameters influencing the tribological properties of nanoparticle-based lubrication systems. Each parameter will be discussed in detail in the following sections.

The Effect of Nanoparticle Size

The effects of nanoparticle size on tribological properties of nanoparticle-based lubricants are three-fold. First, the size of nanoparticles determines their intrinsic mechanical and physicochemical properties that, in turn, influence their tribological properties. For instance, the hardness of materials increase with decreasing grain size due to increased number of dislocation pileups

for crystals in the size range of 100 nm or higher (Hall-Petch regime) [19-21]. In this regime, the hardness increases linearly with the inverse square root of solid size. At the critical grain size, typically below 10 nm, nanomaterials become softer with decreasing size (Inverse Hall-Petch regime) [21-23]. When nanoparticles that are harder than shearing surfaces are placed between these shearing surfaces, they indent and scratch the surfaces. Thus, the size induced variations in hardness of nanoparticles must be kept in mind while designing nanoparticle-based lubrication systems.

Usually below 50 nm, the melting temperature of a nanoparticle sharply decreases with decreasing size [24-27]. For example, while the melting point of bulk CdS is about 1600 °C, 2-nm CdS nanoparticles melt at 400 °C [27]. Such size-dependent melting depression of nanomaterials needs to be considered during the design of nanoparticle-based lubricants to ensure that the nanoparticles used for the lubrication of engines and machines do not melt at the typical operation temperature ranges of the engines and machines.

Second, when nanoparticles squeeze out of the contact region upon loading and shearing, the shearing surfaces do not gain any tribological benefit from nanoparticles [28]. In other words, nanoparticle-based lubrication systems need to stay in the contact zone during loading and shearing to protect shearing surfaces. From this standpoint, the effect of nanoparticle size can come into play when we consider that the asperities of shearing surfaces can act as physical barriers that keep nanoparticles within the contact zones. To illustrate this effect, let us consider two different conceptual cases. The first case is that when the characteristic roughness length scale of shearing surfaces is smaller than the radius of the nanoparticles, the ratio of rms roughness to the radius of nanoparticle is an indicator of how much lateral force is required to dislodge a nanoparticle out of an asperity barrier (Figure 1). This

*Corresponding author: Mustafa Akbulut, Artie McFerrin Department of Chemical Engineering, Materials Science and Engineering Program, Texas A&M University, 230 Jack E. Brown Engineering Building, 3122 TAMU, College Station, TX 77843-3122, USA, E-mail: mustafa.akbulut@chemmail.tamu.edu

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means that if the nanoparticles are too large and non-adhering, they can easily escape from the contact zone and lead to poor lubrication. In the second case, when the characteristic roughness length scales are much larger than the radius of the nanoparticles, the valleys between asperities of the shearing surfaces can be filled with nanoparticles, i.e. nanoparticles artificially smooth out the shearing surfaces and, hence, can improve the tribological properties (Figure 1).

Third, homogeneity of lubricant formulation that strongly controls its ability to perform reliably and smoothly is strongly influenced by colloidal stability. The rate at which nanoparticles settle out of dispersions is an important parameter determining colloidal stability, and can be calculated using Stokes' law [29].

$$v_z = \frac{2(\rho_{NP} - \rho_F)gr^2}{9\mu} \tag{1}$$

v_z is the settling or terminal velocity, ρ is density (the subscripts NP and F indicate nanoparticle and fluid, respectively), g is gravity, r is the radius of the particle, and μ is the dynamic viscosity of the fluid. This equation indicates that for a given base-oil fluid, when the size of nanoparticle additives decreases 10-fold (e.g., 100 nm instead of 1 μ m), sedimentation time will increase 100-fold. This simple calculation illustrates potential improvement in the stability of nanoparticle dispersion through decreasing particle size.

The Effect of Nanoparticle Shape

The shape of nanoparticles used in lubricant additives is another important parameter to consider in the context of designing nanoparticle-based lubricants. The shape of the nanoparticles directly determines the pressures experienced by nanoparticles upon loading. For instance, for a given load, nanospheres experience the largest pressure and nanosheets experience the smallest pressure, because while nanospheres make point contact with a counter surface, nanoplatelets make a planar contact (Figure 2). Thus, for a given load, nanosheets have the least chance of indenting and deforming the asperities of shearing surfaces.

The Effect of Nanostructure

The internal nanostructure of nanoparticles can influence their mechanical properties and therefore also their tribological properties. For instance, vacancies within nanomaterials act as pinning centers inhibiting dislocation motion, thereby enhancing the mechanical strength within a certain concentration [30,31]. Thus, the presence of a limited amount of atomic vacancies can enhance the mechanical strength of the nanomaterials and could be desirable from a tribological perspective. However, excessive amounts of cavities are disadvantageous for the mechanical strength of the nanomaterials. For example, the Young's modulus of a defected nanotube is gradually reduced with each atomic defect, and the plastic strength of the

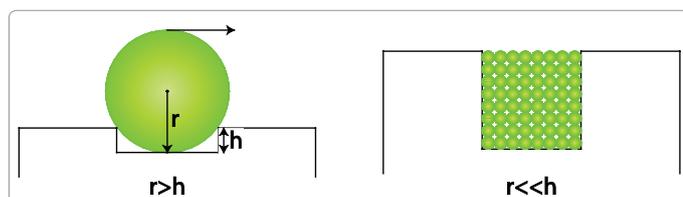


Figure 1: The effect of surface roughness on the organization of nanoparticles between the asperities of shearing surfaces.

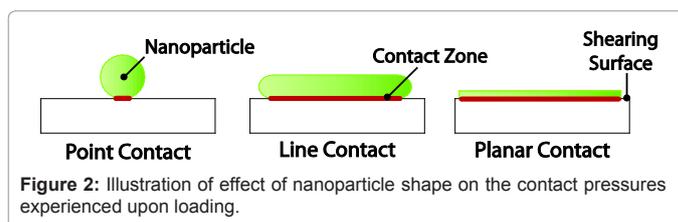


Figure 2: Illustration of effect of nanoparticle shape on the contact pressures experienced upon loading.

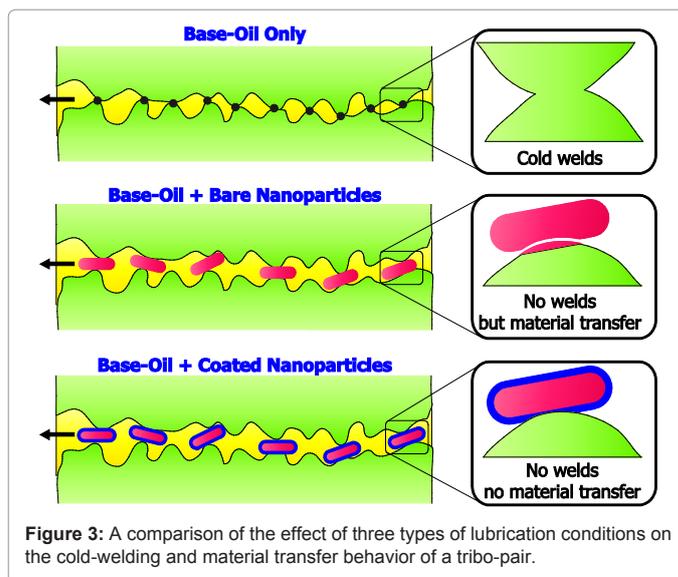


Figure 3: A comparison of the effect of three types of lubrication conditions on the cold-welding and material transfer behavior of a tribo-pair.

nanotubes is dramatically influenced by the existence of just a few atomic defects [32,33].

Another example illustrating the significance of nanostructure is inorganic nanoparticles of layered compounds with a hollow polyhedral structure, known as fullerene-like nanoparticles (IF) [34]. Such nanoparticles have been shown to have excellent tribological properties [35]. This can be attributed to: (i) their polyhedral shape which allows them to roll and slide between shearing surfaces, and (ii) their layered structures, which act as reservoirs which cover the mating surfaces with low friction thin layers when they break down and experience material transfer [36].

The Effect of Surface Functionalization

Surface functionalization plays two different roles in the context of nanoparticle-based lubricant formulations; it regulates colloidal stability of nanoparticle dispersion and enhances the lubricity of the nanoparticles' outer most layers.

First, bare or uncoated nanoparticles of metals, metal oxides, ceramic materials, and chalcogenides, have strong van der Waals forces and tend to aggregate in inert nonpolar liquids, such as hydrocarbon [37]. Aggregation is typically prevented by protecting nanoparticles via steric stabilization, which usually involves coating the nanoparticles with a tightly bound polymer or surfactant monolayer [37]. Basically, surface functionalization is a prerequisite when the enhanced colloidal stability and homogenous distribution of nanoparticles in base-oil are required.

Second, surfactant-coated nanoparticles generally have better lubricating properties than bare nanoparticles in oils for two key reasons. The first reason is that bare nanoparticles experience material

transfer when they come into direct contact with shearing surfaces while they prevent cold-welding of shearing surfaces. On the other hand, the surfactant-coated nanoparticles prevent both material transfer among the nanoparticles and cold-welding between the shearing surfaces. The second reason is that the surfactant-coated nanoparticles have a hybrid structure, with a hard interior and a soft exterior. This synergistic combination provides nanoparticles with a rigid shape and a slippery fluid-like surface. This allows for a high load carrying capacity while not trading off any lubricity.

The Effect of Nanoparticle Concentration

Previous studies have indicated that the concentration of nanoparticles within base-oil strongly influences the tribological properties of such lubrication systems [6]. In general, there is an optimum concentration at which the coefficient of friction is at a minimum. However, the optimum concentration is strongly system dependent, in that the lubricant formulation needs to be tuned for each operation condition.

Overall, designing a nanoparticle-based lubrication system is a very complicated process governed by multiple parameters. The relative importance of these parameters is mostly unknown. To advance the current state of knowledge in the field of nanoparticle lubricants, synergistic approaches involving experimental and theoretical efforts are needed.

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