

# A Review on the Effect of Metal Oxide Nanoparticles on Tribological Properties of Biolubricants

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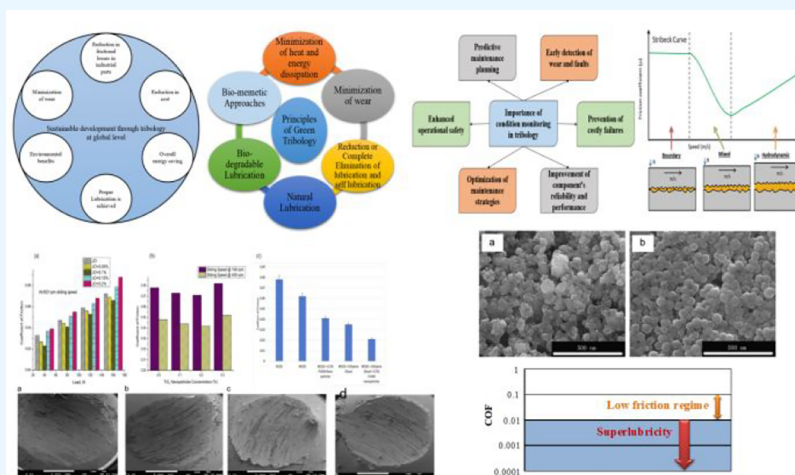
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**ABSTRACT:** This review provides a comprehensive and accessible literature review on the integration of nanoparticles into biolubricants to enhance wear and friction regulation, thus improving the overall lubricated system performance. Nanotechnology has significantly impacted various industries, particularly in lubrication. Nanobiolubricants offer promising avenues for enhancing tribological properties. This review focuses on oxide nanoparticles, such as zinc oxide (ZnO), aluminum oxide (Al<sub>2</sub>O<sub>3</sub>), copper oxide (CuO), titanium dioxide (TiO<sub>2</sub>), zirconium dioxide (ZrO<sub>2</sub>), and graphene oxide (GO) nanoparticles, for their ability to enhance lubricant performance. The impact of nanoparticle concentration on biolubricant properties, including viscosity, viscosity index, flash point temperature, and pour point temperature, is analyzed. The review also addresses potential obstacles and limitations in nanoparticle incorporation, aiming to propose effective strategies for maximizing their benefits. The findings underscore the potential of nanobiolubricants to improve operational efficiency and component lifespan. This review aims to provide valuable insights for researchers, engineers, and professionals in exploring and leveraging nanotechnology's potential in the lubrication industry. This review paper explores the basics of tribology along with its significance, green principles, mechanisms, and energy savings because of friction, wear, and lubrication. Condition monitoring techniques are also explored to achieve brief knowledge about maintaining reliability and safety of the industrial components. Recent advances in tribology including superconductivity, biotribology, high-temperature tribology, tribological simulation, hybrid polymer composite's tribology, and cryogenic tribology are investigated, which gives a thorough idea about the subject.

## 1. INTRODUCTION

Tribology is basically a study of the relative motion of interacting surfaces, remarkably their friction, wear, and lubrication.<sup>1,2</sup> In many applications, particular oils are used to control and manage friction and wear by lubricating the contact surfaces like bearings, gears, seals, etc.<sup>3–7</sup> The vegetable oils are favored over mineral oil as a lubricating base oil due to their excessive biodegradability, renewability, and low toxicity.<sup>8,9</sup> Biolubricants synthesized from vegetable oils are obtained from plant vegetables, fruits, seeds, and leaves. These are effectively used in pharmaceutical products, cosmetics, soaps, and shampoos.

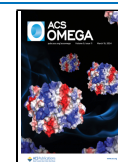
These plant-based bio-oils are composed of triglycerides, phytosterols, natural pigments, phospholipids, and fatty acids.<sup>10</sup> A lubricant provides a defensive film between the

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contacting surfaces to avoid the friction and wear to some extent.<sup>11</sup> Figure 1 shows the basic classification of lubricating oils.

LUBRICATING OILS			
Mineral Oil	Synthetic Oil	Semi-Synthetic Oil	Bio-Lubricants
<ul style="list-style-type: none"> <li>• Paraffinic</li> <li>• Napthenic</li> <li>• Aromatic</li> </ul>	<ul style="list-style-type: none"> <li>• Synthetic Hydrocarbons</li> <li>• Silicon Oil</li> <li>• Organohalogen</li> </ul>	<ul style="list-style-type: none"> <li>• Mixture of Mineral Oil and Synthetic Oil</li> </ul>	<ul style="list-style-type: none"> <li>• Animal Oil/ Fish Oil</li> <li>• Vegetable Oil</li> <li>• Synthetic Esters</li> <li>• Organic Waste Oil</li> </ul>

Figure 1. Classification of lubricating oil.<sup>12–14</sup>

Apart from solid and liquid lubricants that are being used rigorously, now-a-days there are intelligent lubricant materials that are being used. Such materials adjust themselves in the changing environment and manifest their functions according to the change that occurred.<sup>15,16</sup> A good lubricant must contain good thermal stability so that it can resist heat which develops during mitigation of contacting surfaces. Also, it should possess a higher Viscosity Index so the lubricant will affect less with variation of temperature. Besides this, a lubricant also must possess a low freezing point and high boiling point, and it should be capable of resisting the oxidation process.<sup>17</sup> Tribological performance is usually associated with lubricity. Lubricity is the formation of a layer of lubricant on the contacting sliding surface. The thickness of this tribo film should be optimum always. High lubricity lowers friction and energy loss by reducing direct contact between surface asperities.<sup>18,19</sup>

In recent years, there has been a constant hunt for sustainable and environmentally friendly solutions for lubrication, and it has driven extensive research into the domain of biolubricants. These biodegradable lubricants which are derived from renewable resources possess certain properties, because of which these are considered as potential candidates for industrial applications. However, it is a key challenge for the researchers to enhance their tribological performance to obtain their full potential.

There are several strategies among those, and incorporation of metal oxide nanoparticles (NPs) into the biolubricants has emerged as a noteworthy approach. Metal oxide nanoparticles own unique physiochemical properties and high surface area, and eventually they have accumulated significant attention as additives to enhance the lubricating performance of biolubricants.

This review paper gives a brief idea of the current state of research on the impact of metal oxide nanoparticles on the tribological properties of biolubricants. The fundamental mechanisms underlying the interactions between nanoparticles and biolubricants were explored along with the tribological behavior of metal oxide nanoparticles like zinc oxide, titanium dioxide, silica, etc. in biolubricants.

## 2. TRIBOLOGY AND ITS SIGNIFICANCE

Tribology is an important branch of science, with several practical uses. It is essential in many industries due to its function in increasing energy efficiency, lowering environmental impact, and improving the dependability of machines. The study of tribology will remain crucial for developing more effective and long-lasting solutions for our changing world as technology

develops. Figure 2 gives a brief description of the advantages of tribology along with its significance.

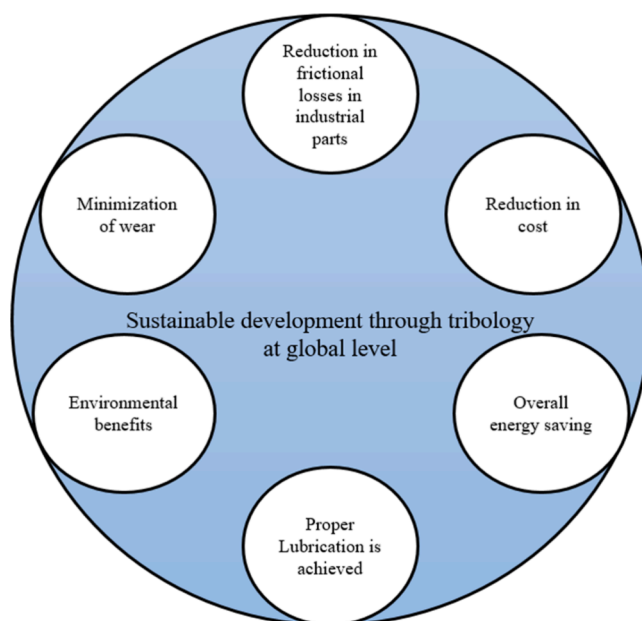


Figure 2. Sustainable development through tribology.

There are several tribological mechanisms which are considered while designing an efficient lubricating system, minimizing wear, and improving overall performance and longevity of mechanical components.<sup>20</sup> Figure 3 lists all of the tribological mechanisms. Adhesive friction and wear mechanism occur when the microsurface asperities adhere to each other, which leads to resistance against the relative motion, whereas abrasive friction and wear are the mechanism which involves the removal of material from one or both of the surfaces because of surface asperities or other hard particles. Fatigue wear mechanism is acknowledged where repeated cyclic loading and unloading occurs, which further leads to crack initiation and propagation.<sup>21,22</sup> Boundary lubrication mechanism is seen where there is a very thin layer of lubricant film and the load is carried by the surface asperities only.<sup>23</sup> Mixed lubrication mechanism occurs in the regime where there are considerable amounts of hydrodynamic effects. It is the intermediate regime of boundary and full films lubrication where lubricant film is not sufficient to separate the two contacting surfaces completely.<sup>24</sup> Hydrodynamic full film mechanism is when the relative motion of the mating surfaces causes the fluid to be drawn into the contact zone, which creates a pressurized thick fluid film between the two contact surfaces.<sup>25</sup> Elastohydrodynamic mechanism involves the combined principles of fluid dynamics and electrostatics. This happens where the film is capable to make the elastic deformations on the surfaces but not that thick to prevent the contact all together.<sup>26</sup>

**2.1. Energy Saving through Tribology.** In recent times, many researchers have outgrown their interest in the field of tribology, with the motive to overcome the loss of energy due to friction and wear. To be more specific, tribological measures are used to reduce energy loss due to friction, wear, and lubrication. Friction and wear are all around where there is movement of components. According to refs 27 and 28 the estimated energy loss due to friction in the industrial sector is 45%; in the transportation sector it is 85%, and in household activities it

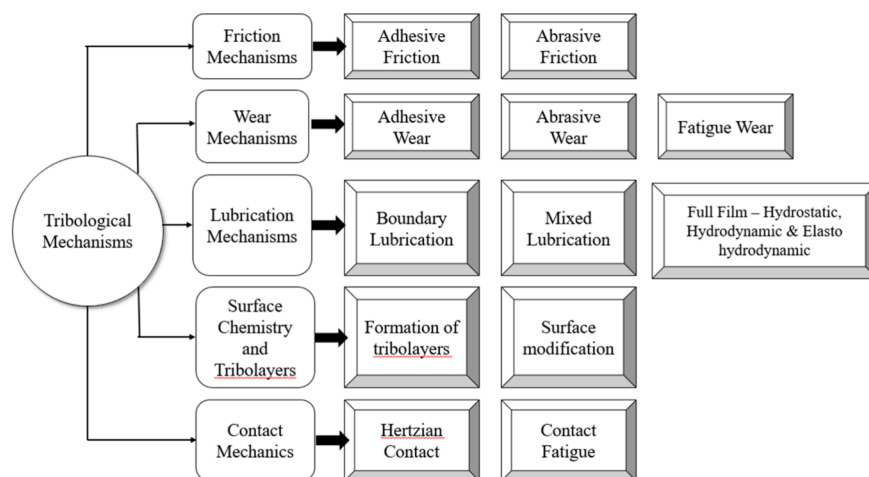


Figure 3. Tribological mechanisms.

accounts for 45%. Globally, 208,000 million liters of fuel is consumed due to these energy losses.<sup>29</sup> The scientists across the world have concluded that 24% of energy is being conserved in USA through tribological measures.<sup>30</sup> Any new advances and developments in tribological methods can lead to saving 11% of energy utilized in transportation, industrial, and other utilities.<sup>31</sup> Advances in nanotechnologies have helped in saving energy by improving the tribological and rheological properties of nanofluids. According to ref 32 a high-speed Taylor-Couette system is being developed to study nanofluids, which reduces power by 58.16% when Al<sub>2</sub>O<sub>3</sub> NPs are synthesized in Water-Based Mud. Several areas of nontraditional tribology have gained the interest of current researchers which include “Tribology for Energy Conservation” and “Environment-Based Tribology”.<sup>33</sup> During the past few years, Green Tribology has come into the focus. The studies about the relative motion of the interacting surfaces that also take energy and environmental sustainability into consideration<sup>34</sup> (Figure 4) summarize the

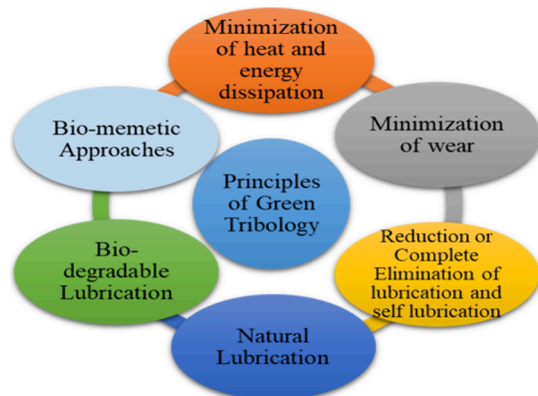


Figure 4. Principles of Green Tribology.

principles of green tribology. According to Jost, H. and Peter Schofield, J., by adopting established principles of Tribology, energy can be saved in the following manner.<sup>35</sup>

- Reduction in energy consumption by lowering the frictional losses.
- Reduction in manpower energy by using proper lubrication.
- Saving through lubricant costs.

- Saving through maintenance and replacement costs.
- Energy savings through losses after breakdown.

**2.2. Condition Monitoring in Tribology.** This term signifies the continuous surveillance of the condition of a machine so as to avoid complete breakdown which eventually leads to production loss, several delays, and increase in cost. It is a well-known fact that condition monitoring is a type of predictive maintenance. Vibration, noise, temperature, etc. are some parameters which are being monitored.<sup>36–39</sup> Figure 5

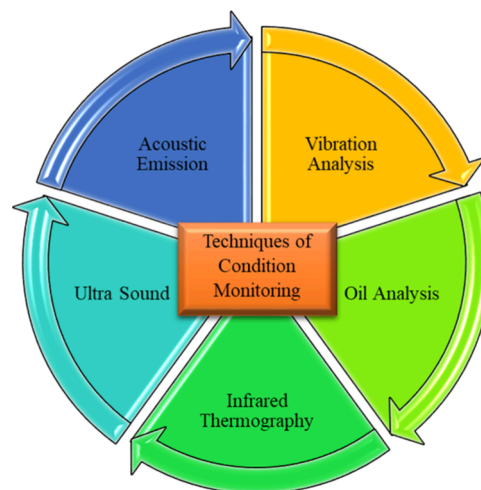


Figure 5. Condition monitoring techniques.

shows a representation of techniques used in condition monitoring. Condition monitoring techniques are helpful for maintaining the reliability, safety, and efficiency of the industrial machinery. It also helps in adopting proactive maintenance strategies, minimizing downtime, and making better decisions about the operations of tribological components. The importance of condition monitoring in tribology lies in its ability to provide valuable insights of the health and performance of machinery and its components where friction, wear, and lubrication are involved. Figure 6 shows some basic importance of condition monitoring.

**2.2.1. Vibration Analysis.** This technique for inspecting the health of the machine and its rotating parts is considered the best

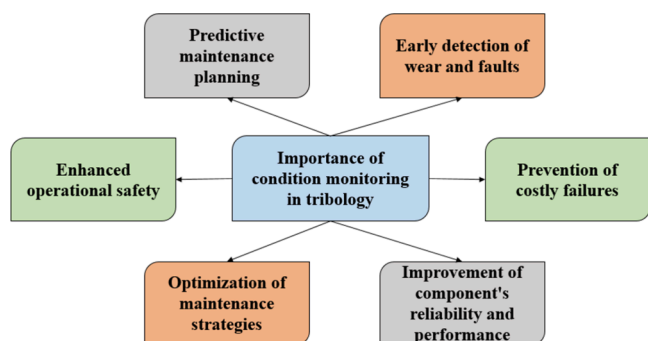


Figure 6. Importance of condition monitoring in tribology.

and most ancient method. Figure 7 shows the various vibrational analysis techniques used.

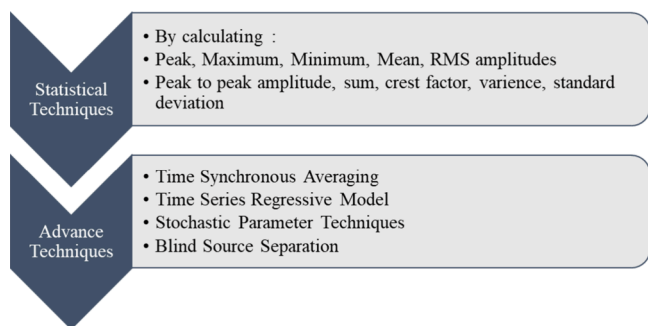


Figure 7. Techniques of vibration analysis.

Internal combustion engines have the tendency to produce very high levels of vibrations due to closures and openings of valves, high-pressure fuel injections, impacts due to clearances, etc.<sup>40</sup> Classical techniques for vibration analysis of IC engines are Spectral analysis, Envelope analysis, and Time-frequency analysis.<sup>41</sup> Artificial intelligence techniques have been used for vibration analysis, for rolling element bearings.<sup>42</sup> Ebersbach, Stephan Peng, Zhongxiao et al. developed an expert system to examine vibrational data with almost the same accuracy when obtained by a vibrational analysis done by an expert maintenance engineer.<sup>43</sup> When machinery is in operation, it generates vibrations that can be generated in terms of amplitude, phase, and frequency. These mechanical vibrations are then converted to electrical signals by accelerometers and other sensors. Vibrations can be continuous or occur at regular intervals. These help in establishing baseline patterns for healthy equipment and identifying deviations.

**2.2.2. Oil Analysis.** It is a type of predictive maintenance in a condition monitoring technique in which the state of oil is being inspected. Lubricant is analyzed frequently at scheduled intervals for contaminants, chemical contents, wear debris, and degradation in quality of oil by finding changes in viscosity.<sup>44,45</sup> Oil samples are being collected from machine at regular intervals, and various analytical techniques are used to evaluate physical and chemical properties of the oil. Oil viscosity, contamination, wear debris, chemical composition, and particle counts are the parameters that are used for analysis and predicting the health of system. Yin Yonghui et al. incorporated integrated an oil analysis condition monitoring technique, in which there is an inductance transducer which detects large ferrous and nonferrous wear debris and a fiber-optic transducer which detects small particles and contamination levels.<sup>46</sup>

**2.2.3. Infrared Thermography.** It is a complete non-destructive method for examining the system by the amount of radiation that is being emitted by its components. It does not require any direct contact and so ended in a harmless and economical process of condition monitoring.<sup>47,48</sup> This method of condition monitoring is proved to be sensitive, noncontact, nonintrusive, and stable to various faults.<sup>49</sup> The infrared thermography technique is used to address dry frictional areas leading to overheating of the mating component which eventually results in component failure, creating a safety hazard hindering productivity.<sup>50</sup>

**2.2.4. Ultrasonic Technique.** This technique of condition monitoring inspects most general mechanical faults, like lack of lubrication, discovering compressed air leaks, identifying electrical problems, locating steam traps, figuring problems in motors, gears and pumps, and arc detection.<sup>51,52</sup>

**2.2.5. Acoustic Emission.** This technique involved detection and analysis of transient stress waves or acoustic emission that is being generated within the material when an external force is applied. Sensors and transducers are used to convert these acoustic signals into electrical. These are helpful in structural health monitoring, material characterization, and monitoring manufacturing processes. A huge series of acoustic techniques have been developed in recent years especially in the water treatment industry, sewage treatment industry, oil manufacturing, and all the industries where transportation of oils is involved. The acoustic technique of condition monitoring investigates blockages, leaks, and depositions. This technique is noninvasive in nature and relies on sound waves.<sup>53,54</sup> Researchers made a comparative study for condition monitoring through vibration analysis and acoustic emission on rotating elements of bearing.<sup>55</sup> As reviewed by ref 56 Figure 8 represents some Acoustic condition monitoring techniques effectively used in water and sewage pipes.

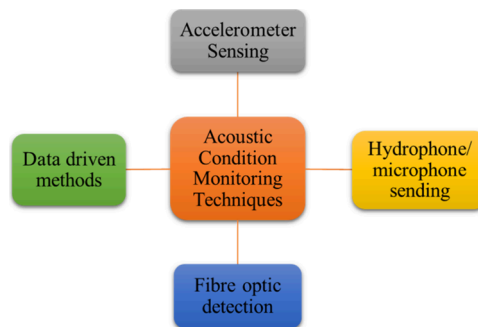


Figure 8. Acoustic condition monitoring techniques.

**2.3. Recent Advances in Tribology.** By increasing effectiveness, dependability, and sustainability of machinery and systems, recent advancements in tribology benefit a number of industries, including automotive, aerospace, energy, and healthcare. Engineers and researchers are constantly looking for new ways to solve problems with friction, wear, and lubrication. Below, Figure 9 depicts the various advances in the area of tribology.

**2.3.1. Superlubricity.** Development of Superlubricity has grown very rapidly in recent years. It is best described as a condition where the friction tends to vanish completely.<sup>57–60</sup> Eventually this mechanism reduces the coefficient of friction (COF) and wear to several extent. Many researchers have concluded that it is that regime of motion where the COF is less

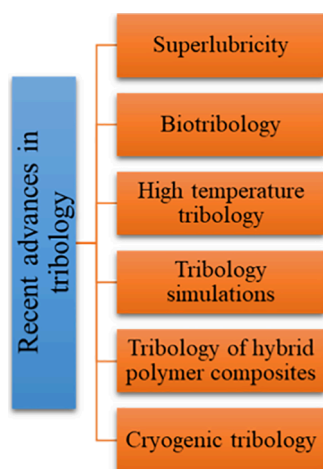


Figure 9. Recent advances in tribology.

than 0.01. Solid superlubricity at micro- and nano levels is easily achieved with 2D materials as in molybdenum disulfide, boron nitride, and graphene. Also, it has been achieved with dissimilar materials like crystalline gold/graphite interface, graphene nanoribbons/gold interface, and silica/graphite interface.<sup>61</sup> According to ref 62, when a nanodiamonds glycerol colloidal solution is used as a lubricant in the steel contact surface of a ball and disk, stable superlubricity with COF of 0.006 is achieved. Figure 10 represents the superlubricity condition.

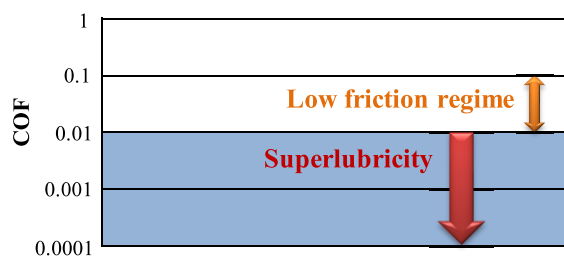


Figure 10. Superlubricity

**2.3.2. Biotribology.** Best described by ref 63, Biotribology is “those aspects of tribology concerned with biological systems”. Medical implant design and evaluation heavily rely on biotribology. Artificial joints, dental implants, and other biomedical devices must be able to withstand the mechanical demands of the human body. Researchers in this area examine the wear and friction characteristics of implant materials and strive to create more robust and biocompatible materials. Specifically in terms of biotribology, contact lenses provide a hurdle. They must offer crystal-clear vision and be cozy to wear for extended periods of time. Improving contact lens design requires an understanding of the interaction between the lens surface and delicate tissues of the eye. Biotribological considerations must be given considerable thought while designing prosthetic limbs and orthotic devices. In order to provide the wearer with long-lasting comfort and functionality, these devices should reduce wear and friction.

**2.3.3. High-Temperature Tribology.** In many applications, the high temperature between the solid contacting surfaces is being accounted. Such applications include aerospace, metal working processes, automotive, and power generation. The high-temperature term is completely cryptic and is fully material-dependent. It means that the high temperature

examined for the polymer will not be high for metals or ceramics. High temperature is clearly that temperature at which oils cannot be used as lubricants.<sup>64–66</sup> Tungsten, molybdenum, and vanadium are some elements which are used to improve high-temperature working stability. So, these are added to alloys for this application as they have a very high melting point temperature.<sup>67</sup> Sajid Alvi et al. have critically analyzed that selective laser-melted stainless steel 316L is a suitable material for high-temperature tribology.<sup>65</sup> Recently cermet materials, which are composites of ceramic and metals, are being used as they exhibit advanced mechanical and tribological properties, especially at elevated temperatures.<sup>68</sup> It has been found out that carbide-free bainitic steel with TiAlN coating is suitable for high-temperature applications for about 800 °C as it has the lowest COF at this temperature.<sup>69</sup> When SiO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and ZrO<sub>2</sub> nanoparticles are being compared for high temperature (930 °C), it has been found out that SiO<sub>2</sub> nanoparticles surpass others by improving the performance of sodium borate as base lubricant. Also, it uplifts the antioxidation by 80%.<sup>70</sup>

**2.3.4. Tribology Simulations.** Simulation is the true replica of an originally existing or proposed mechanism. It enables the testing of the system in various operating conditions and in different scenarios, resulting in the prediction of the future of the system.<sup>71–73</sup> Below, Figure 11 represents the simulation stages.<sup>74</sup>

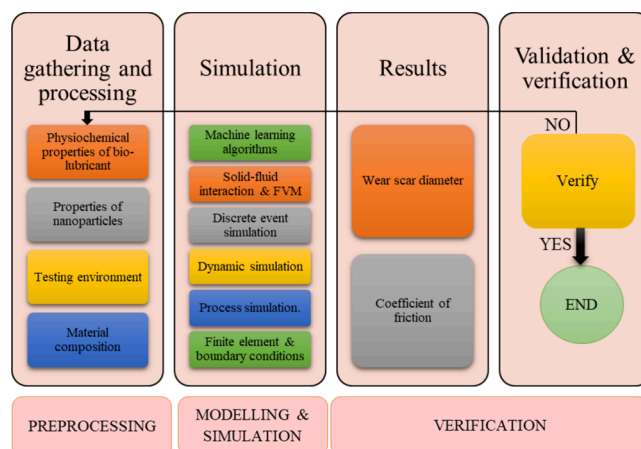


Figure 11. Simulation in tribology.

**2.3.5. Tribology of Hybrid Polymer Composites.** Polymer Tribology is the branch of tribology that deals with the abrasion, adhesion, shear, deformation, and fatigue of polymer materials when they are in frictional contact.<sup>75–81</sup> Hybrid polymers are nowadays used in a wide range of tribological applications, because of their self-lubricating capabilities, acceptable range of wear resistance, low frictional behavior, and good corrosion stability.<sup>82</sup> When 5% carbon nanotubes were incorporated into polymer fiber reinforced materials to make it a better performance hybrid composite, it has been found out that its wear rate decreases but COF increases.<sup>83</sup> Figure 12 represents the tribology associated with a hybrid composite material.

**2.3.6. Cryogenic Tribology.** It is that branch of tribology that deals with the study of friction, wear, and lubrication at extreme low temperature.<sup>84–86</sup> Oxygen, nitrogen, and argon are some cryogenic liquids which are used in medical and industrial applications. Also, in the fast freezing of foods and preservation of some biological items, cryogenic liquids are being used.<sup>87,88</sup> According to Wang et al., the COF of invar 36 alloy and Si<sub>3</sub>N<sub>4</sub>

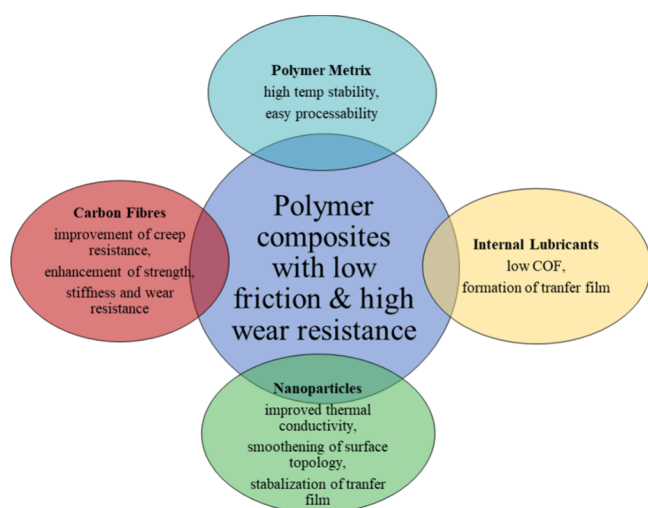


Figure 12. Tribology of the hybrid polymer composite.

ceramic balls has been found to decrease with the temperature. Specifically, it was estimated that below temperature  $-78\text{ }^{\circ}\text{C}$ , the COF value was less than 0.2. When further investigated at  $-196\text{ }^{\circ}\text{C}$  temperature, the wear was very weak. The results concluded that on comparing with G95Cr18 steel, invar 36 alloy showed better tribological behavior under cryogenic conditions.<sup>89</sup> On comparing Minimal Quantity Lubrication, carbon dioxide, and liquid nitrogen as cooling environments it has been found out as a result of experiments that cryogenic cooling is best for tool life enhancement with good tribological characteristics; that is, LN2 cooling effectively helped in tool flank wear reduction of 52.6%.<sup>3</sup>

### 3. BIOLUBRICANTS: NATURE AND CHALLENGES

Biolubricants are nontoxic and easily degradable oils which do not create any harm to nature and all the species.<sup>90</sup> Also they are very less toxic, high viscosity index (VI), high ignition temperature, excellent COF, low evaporation rates, and low emissions into the atmosphere.<sup>91</sup> According to reports, 95% of total lubricants used are petroleum-based, generally termed as mineral oils. These oils are hybrid mixtures of paraffinic (linear/branch), olefinic, naphthenic, and aromatic hydrocarbons of 20 to 50 carbon atoms.<sup>92</sup> Table 1 depicts some biolubricants along with their properties and potential applications.

It has been found out by many researchers across the globe that a major part of the total energy is being lost due to tribological consequences. To be specific, energy losses occur through friction and wear. The foremost solution to controlling friction and wear is by providing proper lubrication between the

contacting surfaces. Lubricants that are widely used in various applications are grease, oils, dry lubricants, and many other petroleum products. It is a well-known fact that petroleum products like diesel, petrol, engine oils, etc. are toxic and nonbiodegradable products, which produce harmful gases after combustion. Also, petroleum is a finite source of energy. These products are one of the causes of acid rain also. These consequences have outgrown the interests of young researchers to find alternative ways to replace such products with less harmful ones. Using biolubricants in industrial applications will help reduce friction and wear, and also unlike previous methods, they are nontoxic, easily degradable, and not harmful to all ecosystems. Apart from these basic advantages, there are many challenges that need to be rectified before efficient use. Biolubricants possess a very limited operating temperature range, less oxidation stability which causes degradation very easily, lack of viscosity range, low pour point temperature, etc. So, in order to overcome these challenges, nanoparticles are being added in biolubricants to achieve amelioration of certain properties. Many researchers have proved that addition of even a very small quantity of nanoparticles has resulted in better amelioration of tribological properties. Nanoparticles are ultrafine particles having very small diameters ranging around 1 to 100 nanometers.<sup>101</sup> Also, they possess a large specific surface area and good surface activity. Nanoparticles are categorized in many ways on the basis of their size, properties, or shapes. The main categories are carbon-based nanoparticles, ceramic nanoparticles, metal nanoparticles, semiconductor nanoparticles, polymeric nanoparticles, and lipid nanoparticles.<sup>102,103</sup> Each type of NP has a different molecular structure and chemical properties. Friction is considered one of the foremost reasons for increased energy consumption in machines. So, addition of nanoparticles to base oils has been studied in order to achieve reduction in friction and wear.<sup>104</sup> Petroleum products like gasoline, diesel, etc. are nonbiodegradable oils and are extremely harmful for the environment as they produce harmful particles during combustion. As a result of their disposal, aquatic as well as many ecosystems are getting polluted. On the other hand, the use of these synthetic oils is enormous because they are suitable for lubrication. As predicted by many researchers, there will be a shortage of petroleum products in the near future. Keeping these effective points in view and as the background of study, the author has concentrated on the study of biolubricants with nanoparticles with a motive to ameliorate tribological properties. So, there is a need to find a substitute which can effectively replace synthetic oil and also will have good lubricant properties. Metal oxide nanoparticles have gained interest in the area of tribology, because of their capability to form different nanostructures including nanoparticles, nano-

Table 1. Biolubricants: Properties and Applications

Sr. No.	Bio lubricant	FPT ( $^{\circ}\text{C}$ )	PPT ( $^{\circ}\text{C}$ )	Viscosity 40 $^{\circ}\text{C}$ ( $\text{mm}^2/\text{s}$ )	Viscosity 100 $^{\circ}\text{C}$ ( $\text{mm}^2/\text{s}$ )	VI	Sustainable Applications	ref
1	Castor oil	298	15.8	220.6	29.72	175.3	<ul style="list-style-type: none"> <li>As flame retardants</li> <li>As controlled release fertilizers</li> </ul>	1,93,94
2	Mahua	238	15	38.4	8.3	200	<ul style="list-style-type: none"> <li>Biodegradable food packaging applications</li> </ul>	1,95
3	Sunflower	174	14	23.9	6.7	264	<ul style="list-style-type: none"> <li>3D printing</li> <li>Ecofriendly plasticizer</li> </ul>	1,96,97
4	Soyabean oil	240	-9	32.93	8.08	219	<ul style="list-style-type: none"> <li>As biofuel in 4 stroke engine when blended with methanol</li> </ul>	98,99
5	Rapeseed oil	240	-12	45.6	10.07	201.6	<ul style="list-style-type: none"> <li>As substrates for bone tissue cultures.</li> </ul>	100

balls, nanorods, nanowires, etc.<sup>105</sup> This review paper presents the study of metal oxide nanoparticles synthesized with different biolubricants with a motive to ameliorate tribological properties.

**3.1. Physicochemical Properties of Biolubricant.** A good lubricant must possess the following properties within the optimum range. Several researchers have worked upon the amelioration of properties in order to achieve better tribological and rheological properties.

**3.1.1. Pour Point Temperature.** Low pour point temperature is desirable for biolubricants as it indicates better operating range.<sup>106,107</sup> The low pour point temperature is due to the presence of unsaturated fatty acids.<sup>108</sup> It is the lowest temperature at which a lubricant stops flowing under gravity and starts to solidify.<sup>109</sup> Attia, N. K. et al. compared biolubricants from vegetable oils. Among sunflower oil, soyabean oil, jatropha oil, and waste oil, jatropha oil showed lowest pour point temperature of about  $-12\text{ }^{\circ}\text{C}$ .<sup>110</sup>

**3.1.2. Flash Point Temperature (FPT).** It is that minimum temperature at which a lubricant starts to vaporize and form a combustible mixture with air.<sup>111</sup> FPT is capable of identifying the fire hazard of fuels and lubricants. It is also used to identify whether the lubricant is a blend of two or more base oils of different viscosities. When safety is considered, a higher flash point temperature is desirable, as it will not ignite when the lubricant is exposed to flame or any other source. Eventually a lower flash point temperature is also dangerous because it will tend to ignite easily.<sup>112</sup>

**3.1.3. Viscosity.** Viscosity is the basic property of a lubricant, which is defined as the resistance provided by the fluid to flow. There are two types of viscosities; dynamic viscosity and kinematic viscosity.<sup>113</sup> Dynamic viscosity signifies the magnitude of force that is being required for lubricant to flow at a specific rate, while kinematic viscosity depicts how smoothly the lubricant is flowing under a specific amount of force. When a lubricant possesses high viscosity, its drag and temperature increase, and when a lubricant possesses low viscosity, it allows direct surface contact which eventually results in increased wear.<sup>114</sup>

**3.1.4. Viscosity Index.** A high value of VI is desirable and kept in view while selecting the biolubricant.<sup>115,116</sup> Viscosity Index signifies the influence in viscosity with change in temperature.<sup>117,118</sup> The VI of tilapia oil was found to be 117 and compared with conventional mineral oil, and it was found that it has far better values than the latter one.<sup>119</sup>

**3.1.5. Coefficient of Friction.** This is a dimensionless number that signifies the amount of resistance present in between the contacting surfaces. Materials with COF less than 0.1 are considered as lubricious materials.<sup>120</sup> According to Kumar, Santosh et al. castor oil when blended with engine oil gives a better result in improving friction and wear characteristics.<sup>121</sup> Waste cooking oil after being synthesized by hydrolyzing, esterification, and several recycling processes resulted in COF of 0.09 which is much better than any crude oil of equal viscosity.<sup>122</sup>

**3.1.6. Boiling Point.** A high boiling point of a biolubricant is desirable as it should not boil away despite ceasing to reduce friction, resulting in the moving parts grinding over one another.<sup>123,124</sup>

**3.1.7. Freezing Point.** A low freezing point will mark the effectiveness in the lubrication properties of a biolubricant, as it will not freeze and solidify. Otherwise, it would increase the friction by solidifying and preventing movement altogether.

**3.1.8. Corrosion Prevention Capability.** A biolubricant must be capable of preventing corrosion. So, to protect engine components from salts, which are basic contaminants of fuels, coating the cylinder liners, walls, piston, etc. and other moving parts with a thin layer of lubrication is done in actual practice. This coating helps to avoid water, which is present in the atmosphere along with oxygen, salts, and other abrasive particles, from coming into direct contact with moving parts.

**3.1.9. Acid Number.** It is a measure of acidity. This number monitors the acid buildup in lubricants due to depletion of antioxidants. Oxidation of the lubricants results in acidic byproducts. High total acid number (TAN) indicates excessive oil oxidation, which leads to the corrosion of contacting surfaces. Monitoring the changes in TAN can help in avoiding damage by changing the oil. When Jajoba oil is synthesized with  $\text{Al}_2\text{O}_3$  nanoparticles, the maximum change in TAN was observed at 0.2% concentration of  $\text{Al}_2\text{O}_3$ .<sup>125</sup>

**3.1.10. Base Number.** It is that property of a lubricant which measures its ability to oppose the acid attacks that were being generated during the operation of lubricating oil. It is measured in mg KOH/gms.<sup>111</sup> It serves the most important purpose of protecting the mating parts from sudden and gradual acid attacks by neutralizing acids and eventually reducing the wear.<sup>126</sup>

**3.2. Industrial Applications of Biolubricants.** With the increase in the price of crude oil along with the deficiency, using environmentally friendly biolubricants is the best alternative. Lubricants other than nonautomotive applications have fewer technical and performance demands, and so there is a way for biolubricants to enter the market through such applications. A biolubricant is easy to dispose that is biodegradable, nontoxic, renewable, and most importantly not emit any greenhouse gases. Researchers have been constantly trying their best to use these biolubricants in industries with greater efficiency. Some of the applications have been discussed below.

**3.2.1. Automobile Industry.** Automotive industries have the largest lubricant consumption. Because of the high-performance capabilities of petroleum products, it is very difficult for alternative lubricants to enter the market. In this sector, the key role of biolubricants is to diminish wear between the moving parts, reduce friction, restrict corrosion, improve sealing, and act as a coolant in the automotive parts where excessive heat is being generated. In the automobile industry, biolubricants can be used as gear box oils, transmission fluids, engine oils, and brake oils as well as special oils like white oils and instrumental oils.<sup>127,128</sup> Karanja seed oil, when processed and blended as biodiesel and biolubricant, is studied on a compression-ignition engine. Studies have found that there is less wear debris as compared to engine oil. This has been done through a condition monitoring technique.<sup>129</sup>

**3.2.2. Process Industry.** Some process industries include cement, glass, mining, oil and gas, pulp and paper, food and beverages, chemical and pharmaceuticals, etc. Concrete release agents are used to prevent the sticking of mold with concrete elements. Rapeseed and soybean oils are used as base oils for such applications.<sup>130</sup>

**3.2.3. Manufacturing Industry.** Industrial oils include oils such as machine oils, compressor oils, metal-working fluids, and hydraulic oils. Diesel oil is being used traditionally as drilling mud, but because of increasing environmental disposal problems, biolubricants are being developed. CAOFAME (chrysohyllum albidum oil fatty acid methyl ester) along with polyol ester and fatty acid monoalkyl ester (FAME) is

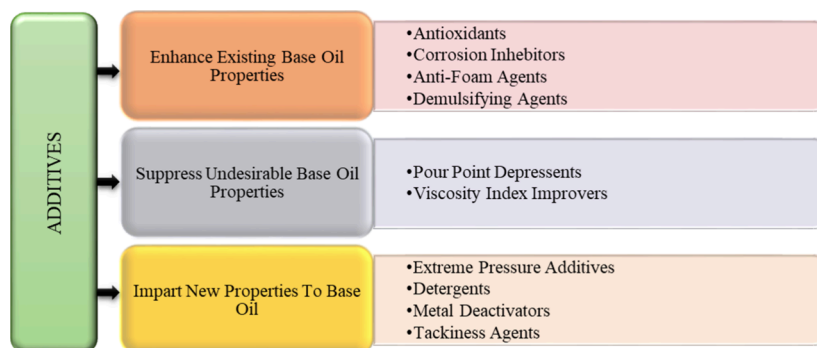


Figure 13. Classification of additives.

blended and tested, and it has been concluded that it is suitable for producing oil-based drilling fluid instead of diesel oil.<sup>131</sup>

### 3.3. Conventionally Used Additives in Biolubricant.

These are chemical substances which are mixed thoroughly in lubricants in order to achieve improvement in lubricating performance.<sup>132</sup> Figure 13 shows the classification of such additives. Some of the traditionally used additives are discussed below.

**3.3.1. Antioxidants.** These additives are specially designed to extend the life of a lubricant by enhancing the oxidative resistance of a base oil. As soon as oxygen comes in contact with the lubricant, oxidation starts, which is the most undesirable phenomenon that causes degradation. Oxidation occurs at every temperature, but it intensifies at higher temperatures and in the presence of water and other metal contaminants. On adding 9% of SK-3 additive in M10 V2 Engine Oil, the total base number (TBN) has raised to 6 from 4.8; also, pour point temperature (PPT) has rose to 224 °C, which indicates that after adding additives, serviceability of lubricant increases.<sup>133</sup>

**3.3.2. Corrosion Inhibitors.** It is a well-known fact that when a metal or alloy comes in contact with a fluid, the surface gets corroded. So, corrosion inhibitors are added to fluids to limit the corrosion rate. When thymus satreoides oil is being used as corrosion inhibitor for 316L stainless steel material in a 3% NaCl solution, experiments have proved that the corrosion rate has decreased with increase in concentration of corrosion inhibitor.<sup>134</sup> Papaya leaves extract (PLE) is an organic corrosion inhibitor which is being tested for copper surface in H<sub>2</sub>SO<sub>4</sub> medium. The result showed that PLE exhibits very good anticorrosion nature over a wide range of temperatures.<sup>135</sup>

**3.3.3. Friction Modifiers.** These are used to minimize the surface contact, eventually reducing the wear and coefficient of friction between the contacting surfaces. There are three types of friction modifiers for liquid lubricants which are used efficiently; organomolybdenum compounds, organic friction modifiers, as well as nanoparticles.<sup>136</sup>

**3.3.4. Anti-Foam Agents.** Anti-foam agents are additives that obstruct the formation of foams in fluids. In order to achieve improvement in tribological properties and the antifoaming performance of silicone oil, it is modified with sulfur and phosphorus elements.<sup>137</sup>

**3.3.5. Demulsifying Agents.** These additives are used to separate two liquids that are immiscible. Magnetic graphene oxide has proved to be a highly efficient and reusable demulsifier for separating oil–water emulsions.<sup>138</sup> Natural lotus leaf after hydrothermal treatment has been used as a demulsifier in rapid breaking of water–oil emulsions.<sup>139</sup>

**3.3.6. Pour Point Depressants (PPDs).** PPD additives help lubricants to sustain low-temperature operating conditions very effectively. Alpha-olefin copolymer with heavy aromatic naphtha is used as a PPD in palm kernel oil as a biolubricant. The results have shown that on adding PPD, the stated biolubricant is capable of withstanding lower temperatures.<sup>140</sup> The addition of ZnO nanoparticles in optimized concentration blended in neem oil prevents the rise in viscosity, clearly manifesting ZnO as a pour point depressant at subzero temperature.<sup>141</sup>

**3.3.7. Viscosity Index Improvers (VIIs).** These viscosity-modifier additives assist oil at high temperatures in becoming very thin. These are incorporated in multigrade engine oils with a motive to eliminate seasonal changing of lubricants. T602HB as VII has been used in ester base oil along with copper nanoparticles, which resulted in improving the kinematics viscosity of lubricant.<sup>142</sup> Quinchia, L. A. et al. studied the behavior of ethylene–vinyl acetate copolymer (EVA) and ethyl cellulose (EC) as viscosity modifiers in vegetable-based oils and concluded that EVA helps in reducing the friction in a mixed lubrication regime, whereas EC when mixed with castor oil effectively reduces friction in mixed and boundary regimes.<sup>143</sup>

**3.3.8. Extreme-Pressure (EP) Additives.** These additives are used to minimize the wear of mating parts when exposed to extremely high pressures. When mineral oil is being characterized with polytetrafluoroethylene (PTFE) as an EP additive, it has been found that the more the concentration of additive in the base oil, the smaller would be the wear scar diameter (WSD) for the same load.<sup>144</sup> Copper oxide and molybdenum disulphite nanoparticles were compared for their capabilities as antiwear (AW) and extreme pressure additives in palm oil. 1.5 times enhancement in AW/EP properties was observed.<sup>145</sup>

**3.3.9. Detergents.** These additives are basic or alkaline in nature. Detergents are used to keep the components clean, and also they neutralize the acids which are formed in the lubricants.

**3.3.10. Metal Deactivators.** These additives are used to avoid the presence of metals like copper in lubricants to perform as an oxidation catalyst.<sup>146</sup>

**3.3.11. Tackiness Agents.** These additives are used to enhance the adhesive properties of a lubricating oil; also, these help in preventing splashing and splattering of oil.

**3.4. Major Biolubricant Manufacturers All over the World.** A promising first step toward a future that is more environmentally friendly and sustainable is the production of biolubricants. Biolubricants are gaining importance in a variety of industries that are attempting to lessen their ecological and carbon footprints by using renewable feedstocks, minimizing environmental effects, and maintaining high performance



Table 2. Top Biolubricant Manufacturers Worldwide<sup>111</sup>

Sr. No.	Manufacturing Organization	Country
4.1	PANOLIN AG	Switzerland
4.2	FUCHS	Germany
4.3	Shell	Netherlands
4.4	Exxon Mobil Corporation	U.S.
4.5	Total	France
4.6	Cargill	U.S.
4.7	Axel Christiernsson	Sweden
4.8	BECHEM	Germany
4.9	Cortec Corporation	U.S.
4.10	Environmental Lubricants Manufacturing, Inc.	U.S.
4.11	Klüber Lubrication	Germany
4.12	Novvi, LLC.	U.S.
4.13	Repsol	Spain
4.14	bp p.l.c.	U.K.
4.15	Emery Oleochemicals	Malaysia
4.16	IGOL	Norway
4.17	LanoPro	Norway

standards. Table 2 shows the top biolubricant manufacturers all over the world.

**3.5. Enhancement of Biolubricant Properties by Nanoparticles.** Incorporating nanoparticles into biolubricants with a motive to enhance their mechanical, thermal, and tribological properties in terms of their performance, stability, and environmental impact is a current area of research of many researchers and scientists. Some potential enhancements include improved lubricity, thermal stability, antiwear properties, oxidation resistance, viscosity modification, and improved dispersion stability. All these enhancements depend upon the selection of appropriate nanoparticles, their concentrations, method of dispersion of nanoparticles into biolubricants, and their mechanisms. Table 3 lists properties of different nanoparticles used. This table is useful for researchers looking for an optimum concentration and synthesis methods of some oxide nanoparticles into biolubricants, so further compatibility study of nanoparticles and biolubricants can be conducted for specific applications.

This paper reviews the effect of nanoparticles with lubricants which are extremely stable, and therefore oxide nanoparticles become viable for various applications like automobile, manufacturing, etc. Unstable nanolubricants may result in the formation of large clusters. These large clusters enter the

Table 3. Properties of the Nanoparticles

SN	Nanoparticle	Particle size (nm), color, morphology	Density (g/cm <sup>3</sup> )	Optimum weight (%)	Applications	Synthesis methods	ref
1	Al <sub>2</sub> O <sub>3</sub>	47.5 ± 2, white, spherical	3.9	1.2	<ul style="list-style-type: none"> <li>• biomedical implants,</li> <li>• catalyst support and absorbents,</li> <li>• fire retardants,</li> <li>• polymer matrix composite,</li> <li>• insulator and in clinical field, electronic fields</li> </ul>	<ul style="list-style-type: none"> <li>• arc plasma,</li> <li>• hydrothermal,</li> <li>• sol–gel, and</li> </ul> Precipitation methods.	147–150
2	ZnO	40, white, spherical	5.812	0.5	<ul style="list-style-type: none"> <li>• Concrete and rubber industries</li> <li>• Gas sensing</li> <li>• Cosmetic and textile industries</li> <li>• Antibacterial, anticancer, anti-inflammatory activity</li> </ul>	<ul style="list-style-type: none"> <li>• Controlled precipitation</li> <li>• Sol–gel</li> <li>• Mechano-chemical</li> <li>• Vapor transport</li> <li>• Solvothermal</li> <li>• Hydrothermal</li> <li>• Emulsion and micro emulsion</li> </ul> Green route	151,95,152
3	CuO	40, brown, spherical	6.341	0.5	<ul style="list-style-type: none"> <li>• In biological applications- Antimicrobial, Antitumor agents, as sensors.</li> <li>• In environmental sensing—heavy metals, toxins and organic pollutants</li> </ul>	<ul style="list-style-type: none"> <li>• Hydrothermal</li> <li>• Solvothermal</li> <li>• Sonochemical</li> <li>• Mechano-chemical</li> <li>• electrochemical</li> </ul>	153,154
4	SiO <sub>2</sub>	20, white, spherical	2.1	0.1	<ul style="list-style-type: none"> <li>• in environmental remediation</li> <li>• catalysis</li> <li>• adsorption</li> <li>• tissue engineering</li> </ul>	<ul style="list-style-type: none"> <li>• Stober method</li> <li>• Reverse micro emulsion</li> <li>• Flame synthesis</li> <li>• Sol–gel</li> <li>• Biogenic synthesis</li> </ul>	155,156
5	TiO <sub>2</sub>	25–55, gray, spherical	4.23	0.3	<ul style="list-style-type: none"> <li>• As reinforcement agents</li> <li>• Photocatalysts</li> <li>• wound-healing material, drug delivery systems, biosensor, and tissue engineering</li> <li>• food preservation</li> <li>• cosmetic</li> <li>• textile</li> <li>• dye-sensitized solar cells.</li> </ul>	<ul style="list-style-type: none"> <li>• Deposition methods – Electrophoretic, Spray pyrolysis</li> <li>• Oxidation methods</li> <li>• Sonochemical and microwave-assisted methods</li> <li>• Hydro/solvothermal methods</li> <li>• Sol–gel</li> <li>• Electrochemical anodization</li> </ul>	157–159

Table 4. Biolubricant with Oxide Nanoparticle: Optimum Weight, Increment, or Decrement in Properties

Sr. No.	Base oil	NP used	Optimum weight	Property of base oil	Original value	Enhanced value	Increment/Decrement	Increment/Decrement in %	Key Findings	ref
1.	Castor Oil	Fe <sub>2</sub> O <sub>3</sub>	0.5% by wt.	Flash Point °C	147	272	↑	85.03%	<ul style="list-style-type: none"> <li>• Fe<sub>2</sub>O<sub>3</sub> has antiwear and friction reducing qualities</li> <li>• Capable of working at high temperatures</li> </ul>	170
				Pour Point °C	-5	-18	↓			
				Viscosity cSt	20	27	↑	35%		
				COF	0.08	0.02	↓	75%		
2.	Karanja oil	TiO <sub>2</sub>	1% by wt.	Viscosity cSt	39.14	37.2	↓	4.95%	<ul style="list-style-type: none"> <li>• increased the load-bearing capacity of base oil</li> <li>• good antiwear and friction reducing capabilities</li> <li>• better flowability and wettability is achieved</li> </ul>	171
				Thermal Conductivity W/mK	0.156	0.165	↑	5.76%		
				Specific Wear Rate (x 10 <sup>-6</sup> ) mm <sup>3</sup> /Nm	5.2	3.5	↓	32.69%		
				COF	0.08	0.055	↓	31.25%		
3.	Rice bran	TiO <sub>2</sub>	1% by wt.	Viscosity cSt	36.4	34.7	↓	4.67%		
				Thermal Conductivity W/mK	0.112	0.121	↑	8.03%		
				Specific Wear Rate (x 10 <sup>-6</sup> ) mm <sup>3</sup> /Nm	6	4.2	↓	30%		
				COF	0.05	0.038	↓	24%		
4.	Madhuca indica (mahua) oil	SiO <sub>2</sub>	0.8% by wt.	Viscosity increment	45%	57%	↑	26.67%	<ul style="list-style-type: none"> <li>• it has high thermal stability, so capable of working where many variations in temperature is there</li> <li>• Capable of working at high temperatures</li> <li>• good antiwear and friction reducing capabilities</li> </ul>	172
				Flash Point °C	145 °C	200 °C	↑	37.93%		
				Pour Point °C	1 °C	6 °C	↑	500%		
				COF	0.1	0.05	↓	50%		
5.	Almond Oil	TiO <sub>2</sub>	0.02% by vol.	Wear scar dia μm (↓)	620	519	↓	16.29%	<ul style="list-style-type: none"> <li>• good antiwear and friction reducing capabilities</li> <li>• good stability and solubility in the bio-lubricant.</li> </ul>	173
				COF (↓)	0.08	0.05	↓	37.5%		

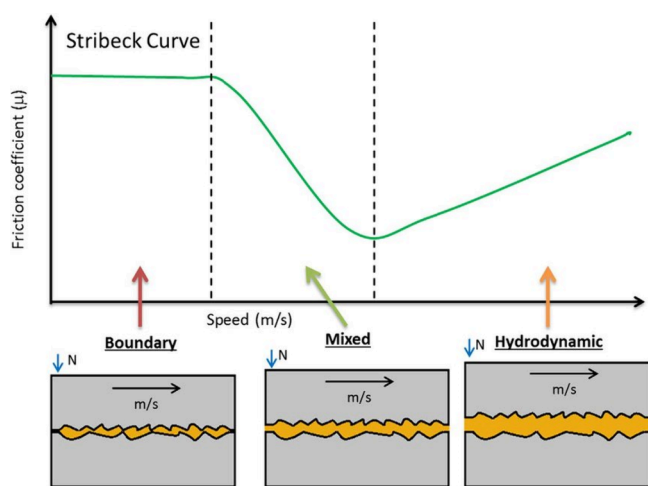


Figure 14. Stribeck curve.

contacting surfaces and become less effective. In addition, the instability of the lubricant results in degrading of properties and decay with time.

**3.5.1. Zinc Oxide (ZnO) Nanoparticles.** These are the most commonly used because of their unique physiochemical properties. This oxide has less toxicity and has a very low effect on human and animal cells. Besides low toxicity, ZnO is preferred because of its low cost, strong adsorption, strong diffusivity, and ultraviolet barrier properties. ZnO nanoparticles have also high surface energy, by virtue of which molecules at the surface when they come in contact will be attracted and will be

strongly bonded.<sup>160</sup> According to Baijing Ren, Liang Gao et al. when ZnO nanoparticles are being modified with oleic acid, they show a better antifriction and antiwear resistance subjected to different loads under lubrication conditions.<sup>161</sup> When raw Euphorbia Lathyris biolubricant oil was compared to the epoxidized biolubricant, its lubricity in terms of friction got improved. This is because of the fact that there is the presence of -O- cross-linking on the surface, which forms a protective film. When further modified by ZnO nanoparticles, it further decreases the friction by forming a defensive film between the surfaces and avoiding direct contact of metals during motion. The raw Euphorbia Lathyris biolubricant oil showed maximum damage on the surface in terms of delamination as compared to the modified biolubricant.<sup>151</sup>

**Aluminum Oxide/Alumina (Al<sub>2</sub>O<sub>3</sub>) Nanoparticles.** Addition of aluminum oxide nanoparticles into lubricating oil results in the formation of a self-laminating protective layer on the contacting surfaces, improving the lubrication properties. Al<sub>2</sub>O<sub>3</sub> nanoparticles also have tendency to convert sliding friction to rolling friction and give lower friction and wear reduction values as compared with base oils.<sup>148</sup>

**3.5.2. Zirconium Dioxide (ZrO<sub>2</sub>) Nanoparticles.** According to Li, Wei et al. by using ZrO<sub>2</sub> and SiO<sub>2</sub> hybrid nanoparticles in lubricating oil, the friction coefficient can be reduced by 16.24% under the optimized concentration of 0.1% by weight.<sup>162</sup> When ZrO<sub>2</sub> nanoparticles were analyzed in automotive lubricant samples it was found out that Wear Scar Diameter (WSD) is reduced by almost 40%.<sup>163</sup>

**3.5.3. Titanium Oxide (TiO<sub>2</sub>) Nanoparticles.** When synthesized with the pure refrigerant R600a, it can save 9.60% of energy

Table 5. Different Nanoparticles Used in Lubrication Oils and Their Effects

Sr. No.	Base Oil	Nano Particles Used	Result Observed	ref
1	Neem Oil	SiO <sub>2</sub>	↓ COF = 0.02 ↓ WSD = 20 mm	187
2	Castor Oil	TiO <sub>2</sub>	↓ COF	
3	Diesel Oil	ZnO	↑Viscosity ↑FPT ↓ PPT	188
4	Epoxidized Euphorbia Lathyris Oil	ZnO	↑Viscosity ↑VI ↑FPT ↓PPT ↓Wear of Pin Newtonian behavior was observed	151
5	Palm oil and Brassica Oil	CuO & TiO <sub>2</sub>	↓ COF when Palm oil +0.5% of CuO	189
6	Diesel Oil	ZnO	↑Viscosity ↑FPT ↓COF	190
7	Diesel Oil	MoS <sub>2</sub>	↑Viscosity ↑FPT ↓COF ↓Mass value of pin	190
8	Diesel Oil	MoS <sub>2</sub> & ZnO	↑VI ↑FPT ↓PPT	190
9	Pongamia Oil	CuO	↓Viscosity by 5.52%	191
10	Engine Oil SAE 20W50	CuO	↑Thermal conductivity coefficient by 3% ↑Flash Point by 7.9%	192
11	Shorea robusta seed oil	CuO	↓Reduction in pin by 4.2% ↑VI ↑Flash Point by 3.42%	153
12	Engine Oil	CuO	↓ COF by 18.4% ↓ WSD by 16.7%	193
13	PAO Oil	CuO	↓ WSD by 14% ↓ COF	194
14	Mineral oil	CuO NP + Graphite MP	↑VI ↑V ↓ COF by 28.5% ↓ Specific wear rate by 70%	195
15	Mineral oil	Al <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub>	At 0.5 wt % -↓ COF = 0.035	196
16	Castrol EDGE professional A5 (5W-30)	Graphene	↓ COF by 28.5% at 0.4% wt. of NP	197
17	Engine Oil	Al <sub>2</sub> O <sub>3</sub> and TiO <sub>2</sub>	↓ COF by 11% at 0.25% wt. of NP ↓ wear rate by 2.6% at 0.25% wt. of NP ↑VI by 1.86%	198
18	Sesame Oil	Spherical TiO <sub>2</sub> & rod shaper ZnO	↓WSD 0.5 wt % of TiO <sub>2</sub> 0.642 to ~0.583 mm ↓WSD 0.4 wt % of ZnO 0.642 to ~0.5773 mm	199
19	Mustard Oil + Coconut Oil	CuO	High viscosity index ~180	108
20	SAE20W40 + Neem Oil, pongamia oil and tamanu oil	Al <sub>2</sub> O <sub>3</sub>	SAE20W40 + Neem oil ↓13.3% COF & ↓55.1% WSD SAE20W40 + Pongamia oil ↓12.8% COF & ↓50.5% WSD	200
21	Oil-in-water based lubricant	TiO <sub>2</sub>	↓ COF by 16.3%	201
22	SAE 50	ZnO	↑ Viscosity up to 12%	202
23	Lubricating Oil	Al <sub>2</sub> O <sub>3</sub> /TiO <sub>2</sub>	At 0.1% wt. of both: ↓ COF by 20.51% ↓WSD by 44%	203

consumption when compared with pure refrigerant. So, using TiO<sub>2</sub> nanoparticles as a nanorefrigerant in domestic refrigerators can improve the performance of these refrigerators.<sup>164</sup> TiO<sub>2</sub> nanoparticles was synthesized with paraffin oil to be used as a nanolubricant; it has been found that it shows a repair effect, as it

mends and fills the rough cracks in metal surfaces resulting in reduction of coefficient of friction.<sup>165</sup>

**3.5.4. Copper Oxide (CuO).** Hernández Battez et al. compared three oxide nanoparticles ZnO, ZrO<sub>2</sub>, and CuO in PAO 6 base oil for their antiwear properties and have concluded

Table 6. Tribometer Specification, Test Environment, and Properties Enhanced

Sr. No.	Lubricants	Nanoparticles	Tribometer	Standards used	Specification of tribometer and test environment	Properties ameliorated	ref
1	Engine Oil	SiO <sub>2</sub>	Pin-on-disk tribometer	ASTM G99, ASTM D6595	Pin dia. =6–10 mm Track dia. =20–50 mm Disc rotation = 1–300 rpm Normal Load 0–100 N Frictional Force 0–100 N	↓ wear rate ↓ COF ↑ flash point Pour Point = no change	155
2	Engine Oil	Al <sub>2</sub> O <sub>3</sub>	Four ball tribometer	ASTM D4172 ASTM D5183	Steel balls = 12.7 mm dia. Test Std. = ASTM D4172, ASTM D5183 Rolling speed = 1200 rpm Oil bath temperature = 75 °C Time = 60 min.	↓ COF ↓ WSD	204
3	Water-Based Lubricant	GO & Al <sub>2</sub> O <sub>3</sub>	Block-on-ring tribometer		Ring diameter = 34.989 mm Siding speed = 100–400 mm/s Normal loads = 10–30 N Room temperatures = 20–25 °C Contact pressure = 70 to 122 MPa	↓ COF ↓ WSD	205
4	Chemically modified rapeseed oil CMRO	CuO, WS <sub>2</sub> , TiO <sub>2</sub>	Four ball tribometer	ASTM D445, ASTM D97, ASTM D92, ASTM D2270, ASTM D287, ASTM D4172	Steel balls = 12.7 mm dia. Rolling speed = 1200 rpm Normal loads = 148 N Oil bath temperature = 75 °C Test Std. = ASTM D4172	CMRO with CuO – better results. ↓ WSD ↑ viscosity	206
5	Jjoba Oil	TiO <sub>2</sub>	Pin-on-disk tribometer	ASTM D 445	Pin dia.=10 mm Pin length = 28 mm Track dia.=90 mm Disc rotation = 150 rpm Temperature = 150 °C Normal loads = 40–100 N Sliding distance = 3000 mm	↑ viscosity ↓ COF ↓ WSD	157

that all of them proved stable in reducing friction and wear. ZnO and ZrO<sub>2</sub> showed similar behavior in reducing friction and wear. 0.5% of ZnO and ZrO<sub>2</sub>, respectively, is optimum to exhibit the best tribological results.<sup>166</sup>

**3.5.5. Silicon Dioxide Nanoparticles (SiO<sub>2</sub>).** When CuO and SiO<sub>2</sub> nanoparticles were being investigated in coconut oil, it was found out that wear volume loss was decreased by 37% and 33% and COF was lowered by 93.75% and 93.25% by using SiO<sub>2</sub> and CuO nanoparticles, respectively.<sup>167</sup>

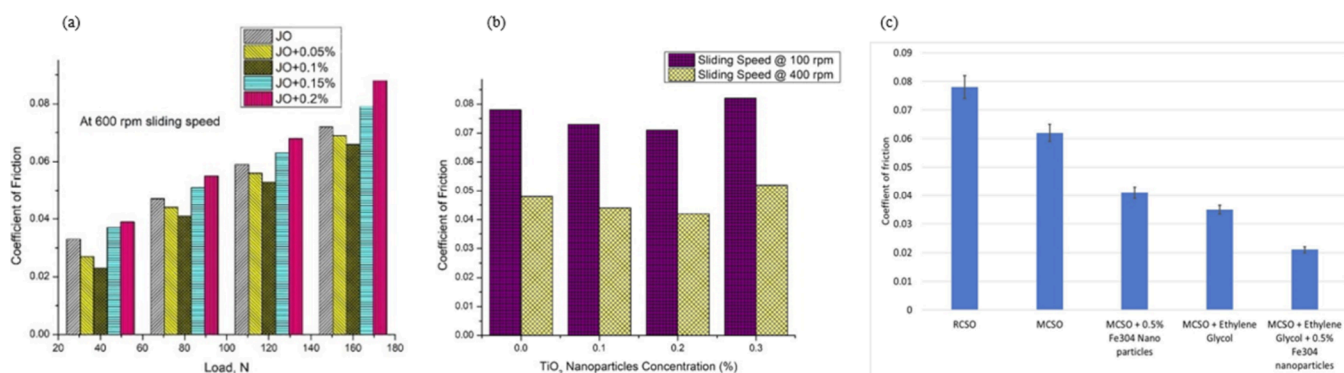
**3.5.6. Graphene Oxide Nanoparticles (GO).** Cashew nut shell liquid is blended with neat castor oil with the aim to replace mineral nonbiodegradable oil. Further GO NPs were synthesized, and it has been observed that there is 61.7% improvement in the performance as compared to commercial mineral oil.<sup>168</sup>

**3.5.7. Cerium Dioxide (CeO<sub>2</sub>).** Cerium dioxide (CeO<sub>2</sub>)–GO/CeO<sub>2</sub> nanohybrid material was incorporated into rapeseed oil; it has been found out that on addition of 0.1% of GO/CeO<sub>2</sub>, the COF decreased by 36.5% and wear rate decreased by 62.4% as compared to neat rapeseed oil.<sup>169</sup>

**3.6. Mechanism of Nanoparticles in Lubrication.** Effectively, there are four effects of the mechanism of lubrication in nano additives, stated as microbearing, protective film, polishing, and repair.<sup>174</sup> The microbearing effect is a situation where the relative sliding friction state is converted into a rolling

friction state when nanoparticles enter the contacting area. Spherical and quasi spherical shaped nanoparticles depict such types of effect.<sup>175</sup> The protective film effect is the most important lubrication mechanism in which, during the sliding condition of contacting parts, nanoparticles tend to form a layer which is reinforced thoroughly. This significantly reduces friction as there is no direct contact of friction pairs; also, shear strength is reduced and results in antiwear performance.<sup>176,177</sup> The polishing effect resulted in reducing the surface roughness of contacting surfaces.<sup>174</sup> As the name clearly depicts, the repair effect of the lubrication mechanism results in filling of cracks or fills by low melting point nanoparticles. According to the Stribeck curve,<sup>178</sup> which gives a brief idea about the lubrication regimes, these regimes are categorized according to the development of lubrication films under different operating parameters, under different loads, and at different contacting surfaces. Eventually three regimes are listed as Boundary, Mixed, and Hydrodynamic.<sup>179</sup>

Boundary lubrication is seen where there is a frequent start stop between the two mating parts. In this regime, the lubrication film is very thin, and the major load is carried by the surface asperities. Here COF is dependent majorly on physical and chemical properties of sliding surfaces.<sup>180</sup> Boundary lubrication leads to catastrophic wear, as there is



**Figure 15.** Graphs showing effect of COF with varying percentage of oxide nanoparticles in biolubricants. (a) Effect of applied load on the friction coefficient & Al<sub>2</sub>O<sub>3</sub> NPs,<sup>125</sup> (b) TiO<sub>2</sub> nanoparticles concentration effect on friction coefficient,<sup>207</sup> (c) COF vs %wt. Fe<sub>3</sub>O<sub>4</sub> of different biolubricant samples.<sup>170</sup>

increased metal contact. Mixed lubrication is the transition between the full film lubrication regime and the boundary lubrication regime.<sup>181</sup> It is that regime where the load is supported by both lubricant film and the contact surface asperities. Piston rings and cams are the most common components of engines and are the best examples of mixed lubrication.<sup>182</sup> In a hydrodynamic full film lubrication regime, the contact surfaces are separated by a thick lubricant which completely avoids direct contact of tool and work piece.<sup>183</sup> Film thickness associated with this regime is 1  $\mu\text{m}$  or more. Also, frictional losses encountered in this are also very less as compared to other regimes.<sup>184</sup> Electrohydrodynamic lubrication is that regime where there is very high contact pressure which causes elastic deformations of surfaces.<sup>185</sup>

From ancient times, nuclear methods have also been used for wear and corrosion measurement. The nuclear reaction-based method using neutron irradiation and the thin-layer activation by accelerated charged particles are the two methods used in various applications worldwide.<sup>186</sup> Table 4 summarizes the overall effect of different nanoparticles used with different base oils in lubrication. Figure 14 shows different lubrication regimes as boundary, mixed, and hydrodynamic.

#### 4. BIOLUBRICANTS TESTING

Testing of lubricants incorporated with nanoparticles is performed on a tribometer, which is used to measure the tribological properties like frictional force, friction coefficient, wear scar diameter, wear volume, etc. Pin-on-disc and ball-on-disc are commonly used tribometers (Table 5). Standards for testing biolubricants have been produced by numerous organizations, including the European Committee for Standardization (CEN) and American Society for Testing and Materials (ASTM) (Table 6). These specifications offer a framework for producers and researchers to guarantee the reliability and security of biolubricants.

**4.1. Testing Specifications. 4.2. Performance of Biolubricants with Oxide Nanoparticles.** As illustrated in Figure 15 (a), 0.1% of aluminum oxide nanoparticles is considered optimum when synthesized with jojoba oil (JO), as minimum COF is observed at different loads. (b) Also, 0.2% titanium dioxide nanoparticles is considered optimum when blended with castor oil. (c) Similarly, on blending modified castor seed oil along with ethylene glycol and 0.5% iron oxide nanoparticles minimum COF  $\sim 0.02$  is noticed. All experimental results show that there is decrease in friction as oxide

nanoparticles are being added in the optimum concentration (Table 7).

As illustrated in Figure 16, WSD was analyzed for different concentrations of NPs; (a) JO when blended with 0.1% Al<sub>2</sub>O<sub>3</sub> NPs at 600 rpm sliding speed at different loads gives minimum WSD hence it can be treated as optimum. Similarly, putranjiva oil blended with CuO NPs gave optimum results at 0.3% wt. concentration.

**4.3. SEM Images of Oxide Nanoparticles.** As nanoparticles tend to agglomerate, there is a prime requirement for surface modification. Afterward they show good dispersion stability in the lubricants. Silane coupling agent (KH-560) is an organosilicon compound which contains an organic and hydrolyzable group. It is used as a surface treatment agent. Figure 17 shows the difference in the aluminum oxide nanoparticles and surface-modified nanoparticles. It can be clearly observed that the latter have the better dispersion stability because of the chemical or physical bonding between KH-560 and hydroxide group.<sup>163</sup>

When the chemically modified palm oil is being characterized by Scanning Electron Microscopy for detailed microscopic views of wear scars, scratched grooves were seen for the bare oils as shown in Figure 18a,b; after the incorporation of copper oxide nanoparticles the scratched grooves were replaced by a smooth surface with minor pits Figure 18c. Figure 18c also showed that CuO NPs were nonuniformly distributed and agglomerations were observed. After introducing surfactant, this problem was resolved, and wear scar diameter was reduced as can be seen in Figure 18d.

#### 5. CRITICAL REVIEW

This paper presents the comprehensive examination of the influence of metal oxide nanoparticles on tribological properties like wear scar diameter, wear volume, and coefficient of friction. It also gives a brief knowledge to readers who are new to the field of tribology. The significance of tribology and its principle along with the condition monitoring techniques which are used as preventive maintenance techniques are included in this review. The literature review is extensive and provides a solid foundation for the study. It is concluded that the addition of oxide nanoparticles up to some optimum concentration is beneficial in reducing friction and wear occurring between the mating parts of machines. A potential reason for this is that the rubbing surfaces experience less friction as a result of the rolling of spherical nanoparticles. One possible explanation for the antiwear mechanism is that oxide nanoparticles were deposited on the

Table 7. Comparative Data between a Biolubricant with NPs Versus a Fully Formulated Mineral or Synthetic Lubricant

Sr. No.	Fully formulated Mineral Oil/Synthetic Oil	Biolubricant	Oxide Nanoparticles	Key Findings	Advantages of biolubricants over fully formulated mineral/synthetic oil	Future Scope	Ref
1.	GL-4 (SAE 75W-85)	Palm oil	CuO	<ul style="list-style-type: none"> <li>• CuO is capable to enhance the antiwear properties by 1.5 times</li> <li>• 2% CuO increased load carrying capacity because of tribo-sintering of nanoparticles onto the surface</li> <li>• After incorporating Al<sub>2</sub>O<sub>3</sub> into engine oil, friction reduction up to 80% and wear reduction up to 50%</li> <li>• Spherical Al<sub>2</sub>O<sub>3</sub> NP prevent direct contact and convert sliding contact to rolling and so helps in improving antiwear properties in extreme pressure condition.</li> </ul>	<ul style="list-style-type: none"> <li>• Improved tribological properties led to better performance</li> <li>• Enhanced wear resistance and load-carrying capacity</li> <li>• Better dispersion of nanoparticles so better lubricating properties</li> <li>• Environmentally safe as derived from renewable resources</li> </ul>	<ul style="list-style-type: none"> <li>• Optimization of particle size, shape and surface characterization</li> <li>• Compatible study for phase separation and aggregation of nanoparticles</li> <li>• Investigation of morphological, structural and chemical changes in biolubricant with Al<sub>2</sub>O<sub>3</sub></li> <li>• Thermal stability and conductivity evaluation at high temperatures for specific industrial applications</li> </ul>	145,194
2.	Engine oil (SAE 10W30)	Neem oil, pongamia oil	Al <sub>2</sub> O <sub>3</sub>				200,209

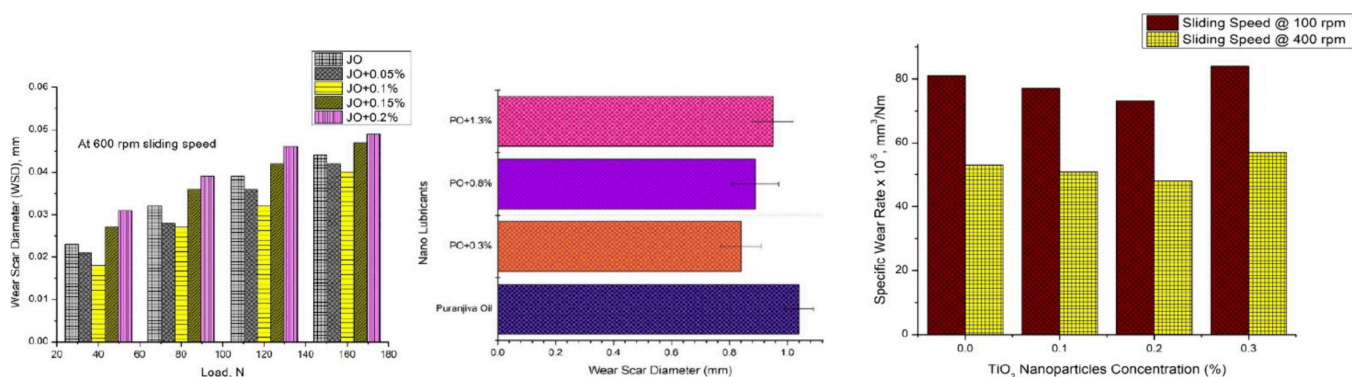
worn surface. Because of this, shearing resistance is reduced, and it improved the tribological characteristics. Thus an oxide nanoparticle-incorporated biolubricant has come out to be a suitable candidate in replacing the mineral-based or synthetic lubricant in industrial applications. This will in turn be saving energy, and it will be a sustainable approach toward the environment. Besides, the experimental techniques which were being employed for studying the tribological properties were being explored. Various aspects of tribology, its significance, energy savings because of tribological aspects, principles of green tribology, and condition monitoring techniques which are beneficial for sustainable applications along with the recent advances in tribology are being explored. This knowledge will help young researchers and beginners who are new in the field of tribology. Conventionally used additives in the biolubricants to enhance various properties were discussed, along with the potential applications of biolubricants. Also, biolubricant manufacturing industries all over the world are being discussed along with the desirable properties of biolubricants.

## 6. FUTURE SCOPE

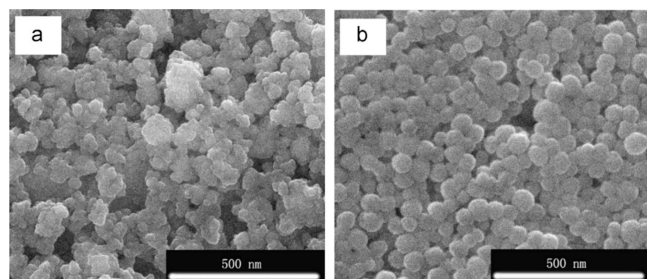
As biolubricants are a nontoxic and easily degradable source of energy, they can be used in various industrial applications as well as in critical areas including lentic and lotic ecosystems. However, many experimental investigations and studies are further needed to be evaluated in order to apply plant-based/animal-fat-based biolubricants in various commercial applications. Research should be carried out for various compatible combinations of biolubricants along with nanoadditives, keeping the focus on the particular application. It is advised to investigate the cost of adding nanomaterials and their effect on toxicity in a future study. Additionally, it is suggested to investigate the ideal volume percent of nanomaterials. Also, it is advised to research how nanomaterial additives affect the lubrication of gear systems and to investigate how using nanolubrication in various gear types can reduce power loss. Metal oxide nanoparticles' tribological properties can be considerably influenced by their size and form. Drawing general conclusions can be difficult, since variations in these features might result in a wide range of results. It is not well-documented how biolubricants containing metal oxide nanoparticles would perform over the long term in a variety of temperatures and operating environments. It is challenging to evaluate their dependability and durability, because of this. The interactions between metal oxide nanoparticles and other additives in biolubricants, which frequently comprise numerous additives, may be complicated and not entirely understood.

## 7. CHALLENGES AND LIMITATIONS

Although the tribological properties of base biolubricants can be greatly enhanced by nanoparticles, they also have some restrictions. The key challenges involved in the area of biolubricants are summarized here. All the thermochemical, physical, mechanical, and tribological properties of biolubricants will majorly depend upon the feedstock, biomass, or any waste material from which base stock's biolubricant is made. Due to potential ecotoxicity and bioaccumulation issues, the use of metal oxide nanoparticles in biolubricants, such as zinc oxide or copper oxide, may cause environmental concerns. The addition of nanoparticles exceeding its optimum concentration may lead to a decrease in the mechanical and tribological properties and eventually decrease its performance. Metal oxide nanoparticle



**Figure 16.** Graphs showing effect on wear behavior with varying percentage of oxide nanoparticles in biolubricants. (a) Effect of applied load on the WSD &  $\text{Al}_2\text{O}_3$  NPs with jojoba oil.<sup>125</sup> (b) WSD for Putranjiva oil with  $\text{CuO}$  NPs.<sup>208</sup> (c)  $\text{TiO}_2$  nanoparticles concentration effect on the wear.<sup>207</sup>



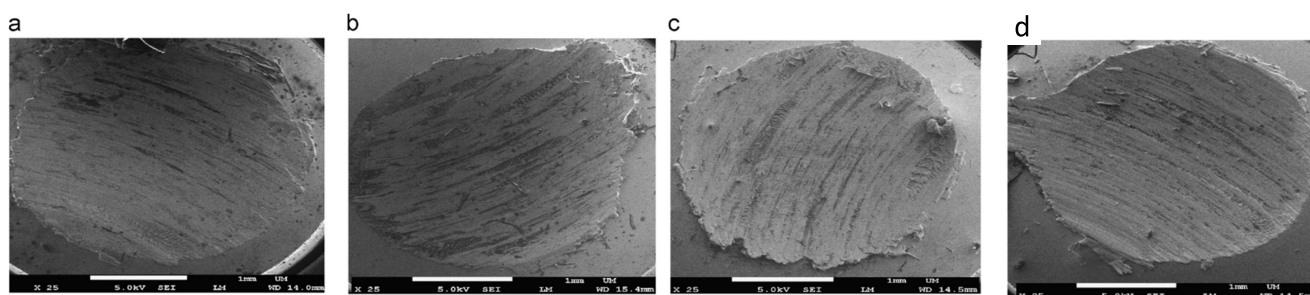
**Figure 17.** SEM images of oxide nanoparticles.

stability and homogeneous dispersion in biolubricants are difficult to achieve. Nanoparticle settling and agglomeration may alter their tribological characteristics at the cost of increasing the COF and wear. It can be expensive to produce metal oxide nanoparticles and incorporate them into biolubricants. Economical difficulties could arise when these processes are scaled up for commercial application. These economical challenges include the cost involved in optimizing the suitable raw material, production efficiency, and also capital cost. The surface modification of the nanoparticles, assuring stability, and performance testing of the new lubricant all incur additional costs. Some metal oxide nanoparticles may not be suitable for some biolubricant applications, because they may have negative health effects or create biocompatibility issues when employed in applications involving contact with live beings.

## 8. CONCLUSIONS

This paper presents an inclusive review on the use of biolubricants along with oxide nanoparticles. The tribological properties like wear scar diameter (WSD), coefficient of friction (COF), viscosity, and viscosity index (VI) were analyzed. It can be concluded that incorporation of oxide nanoparticles in biolubricants in an optimum quantity is a good alternative for ameliorating lubrication performance. Also, it can be stated from literature that nanobiolubricants have the potential to provide better lubricating properties than conventionally used mineral-based oils. For example, when coconut oil was investigated using  $\text{CuO}$  NPs, it was found that wear volume and COF both decrease by 37% and 93.75%, respectively. Further, different additives which were traditionally used for enhancement of properties of base oil were being analyzed. For example, papaya leaf extract is a biobased organic corrosion inhibitor for copper surface in sulfuric acid. Principles of green tribology were being studied, which are helpful for conserving energy through tribological consequences. Various condition monitoring techniques were explored in order to provide brief knowledge on maintenance of the machine to avoid unusual breakdowns. Recent advancements in tribology were being studied, which shows that there has been rapid growth in the field of tribology. Superlubricity with diamond-like carbon (DLC) coatings and many 2D materials have a scope of research and tend to have lower COF. The following are the noteworthy points that can be concluded from this review paper:

- The use of biolubricant as a fuel in vehicles is a bit challenging, but it can be efficiently used as gear oil,



**Figure 18.** Scanning electron microscopic images of wear scars of palm oil, with surfactant and  $\text{CuO}$  nanoparticles. (a) SEM image of wear scar of chemically modified palm oil (CMPO), (b) SEM image of wear scar of chemically modified palm oil (CMPO) with 1% surfactant, (c) SEM image of wear scar of chemically modified palm oil (CMPO) with 1%  $\text{CuO}$  nanoparticle, (d) SEM image of wear scar of chemically modified palm oil (CMPO) with 1% surfactant and 1%  $\text{CuO}$  nanoparticle.<sup>141</sup>

engine oil, compressor oil, brake oil, etc. in various commercial applications.

- As the VI of nanobiolubricants gets increased, this could improve the economy as the consumption of fuel gets decreased.
- On adding nanoparticles into the base lubricant, viscosity gets improved, which leads to the improvement in wear and frictional properties because there is no direct contact of surface asperities.
- Biolubricants have the potential to decrease the environmental impact, as these are very easily degradable and emit no harmful pollutants.

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### Notes

The authors declare no competing financial interest.

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