Suggested Citation

M. Gulzar, H.H. Masjuki, M.A. Kalam, M. Varman, NWM Zulkifli, R.A. Mufti, Rehan Zahid "Tribological performance of nanoparticles as lubricating oil additives" J Nanopart Res (2016) 18: 223.

Tribological Performance of Nanoparticles as Lubricating Oil Additives

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Abstract:

Research into lubricant formulations and lubricant additives has undergone a paradigm shift with advent of nanomaterials. In literature, variety of nanoparticles as lubricant additives have been used with potentially interesting friction and wear properties. To date, although there has been a great deal of experimental research on nanoparticles as lubricating oil additives, many aspects of their tribological behavior are still not yet fully understood. With growing number of possibilities, the key question is: what types of nanoparticles act as better lubricating oil additive and why? To answer this question, this paper reviews main types of nanoparticles which have been used as lubricants additives and out-lines the mechanisms by which they are currently believed to function. Significant aspects of their tribological behavior like dispersion stability and morphology are highlighted.

Key words: nanolubricant, nanoparticles, tribological performance, dispersion stability, lubrication mechanisms, tribo-testing

1. Introduction:

As existing lubricants reach their performance limits, one of the significant scientific tasks is to develop new lubricant formulations that achieve energy efficiency across a multitude of fields, for use under increasingly severe conditions (Akbulut 2012). Instead of traditional materials, this quest of energy efficiency is leading the research towards new materials to be used as lubricant additives. In this regard, nanomaterials and nanoparticles have been recently under investigation as lubricant additives (Bakunin et al. 2005; Bakunin et al. 2004; Kheireddin 2013; Li et al. 2006; Rapoport et al. 1997; Wang and Liu 2013). In the development history of lubricant additives, nanoparticles are a relatively new class of lubricant additives as mentioned in **Fig. 1**. Nanolubricants usually consist of a base oils or fully formulated lubricants with colloidal solid particles suspended within them (Martin and Ohmae 2008; Saidur et al. 2011). There are usually three components in a nanolubricant which are; the solvent which is a lubricant/base oil, the nanoparticles which act as antiwear/extreme pressure (EP) additive or friction modifier and the surfactant that inhabits the interface area between the lubricating oil and the particles (Ohmae et al. 2005). There are many reasons for use of nanoparticles as a lubricant additive. First and main is their tiny size. Due to their tiny size, nanoparticles may enter the contact area, which can result in a positive lubrication effect (Demas et al. 2012; Ghaednia 2014). Also they are small enough to pass undisturbed through filters used in oil systems (Ghaednia 2014; Spikes 2015). Hugh Spikes (Spikes 2015) has mentioned five potential advantages of using nanoparticles as lubricant additives: (1) insoluble in non-polar base oils; (2) less likely to react with other additives in lubricant; (3) high possibility of film formation on many different types of surface; (4) more durable (5) highly non-volatile so able to withstand high temperatures. Different nanoparticles have versatile characteristics and many researchers have reported single type of nanoparticle served the multipurpose as antiwear, EP additive as well as friction modifier (Chou et al. 2010; Hu et al. 2002; Nallasamy et al. 2014; Thakur et al. 2016; Verma et al. 2008). Due to various types, size and morphology of nanoparticles, the combinations of nanoparticles and lubricants can result in several nanolubricants. Although various studies have shown remarkable tribological improvement for lubricants dispersed with different type of nanoparticles, the selection of suitable nanoparticle additive is still very difficult. The effectiveness of nanoparticles depends on various factors including, the compatibility with base oil/ lubricant, nanoparticles size and morphology, as well as additives concentration (Peña-Parás et al. 2015). To answer the question of suitable nanoparticle and lubricant combination, a comprehensive review is required to address all these parameters while focusing their tribological test conditions and related lubrication mechanisms. In this regard, recent reviews (Ali and Xianjun 2015; Dai et al. 2016; Shahnazar et al. 2016) provide an excellent overview of tribological essence of nanoparticles type, morphology and size but lacks the significant information and role of lubricant/nanoparticle compatibility, range/optimum nanoparticles concentrations and test conditions (geometry, load, contact, temperature, speed and time).

Keeping in view the compatibility in terms of dispersion stability and role of nanoparticles morphology and concentration on tribological performance, this article is an effort to consolidate relevant data in organized and apprehensible manner. This paper also provides summary of the relevant material properties, lubricants, test equipment, tribo-test conditions, and characterization techniques by different researchers in their experimental studies.

2. Classification of nanoparticles:

Nanoparticles have different types based upon their applications. As this review is considering the studies related to tribological performance of nanoparticles, therefore the classification has been provided on the basis of widely used nanoparticles for tribological performance. **Fig. 2** shows the three major types of nanoparticles in which engineered nanoparticles have been further classified in eight major types by authors on the basis of their vast use in lubricants.

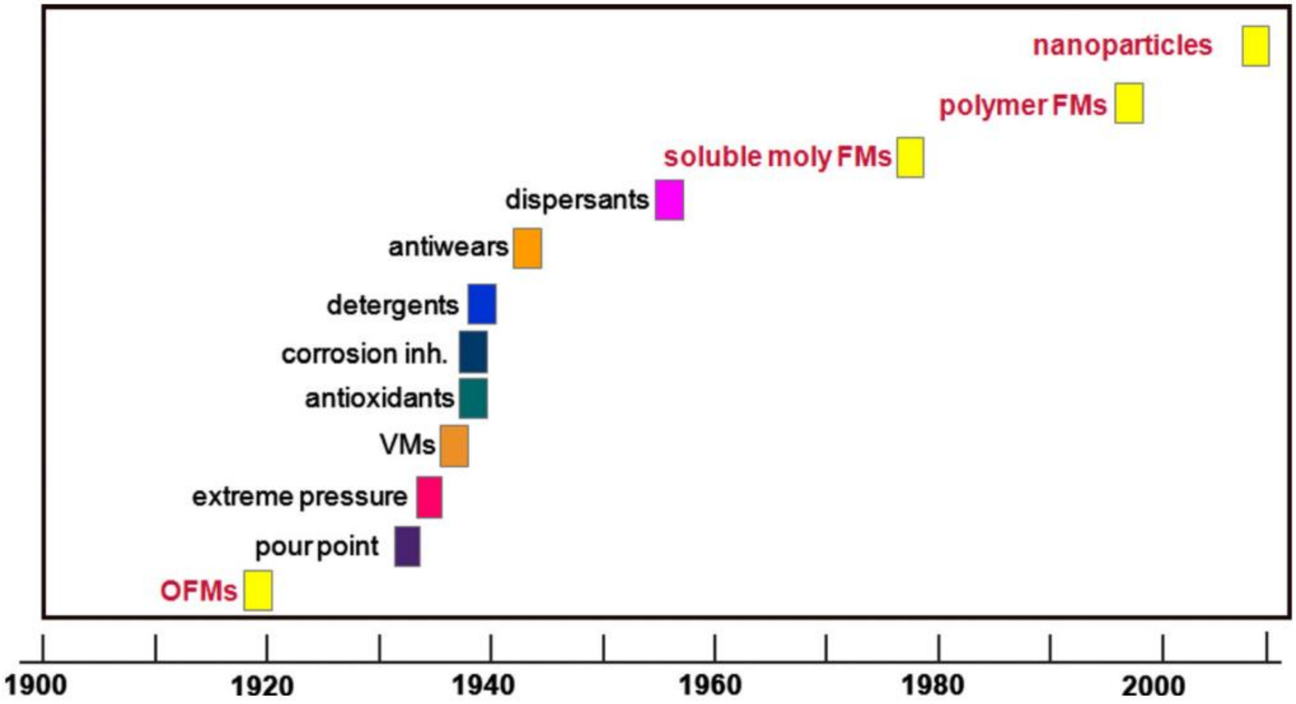


Fig. 1. Timeline for development of lubricant additives (Spikes 2015).

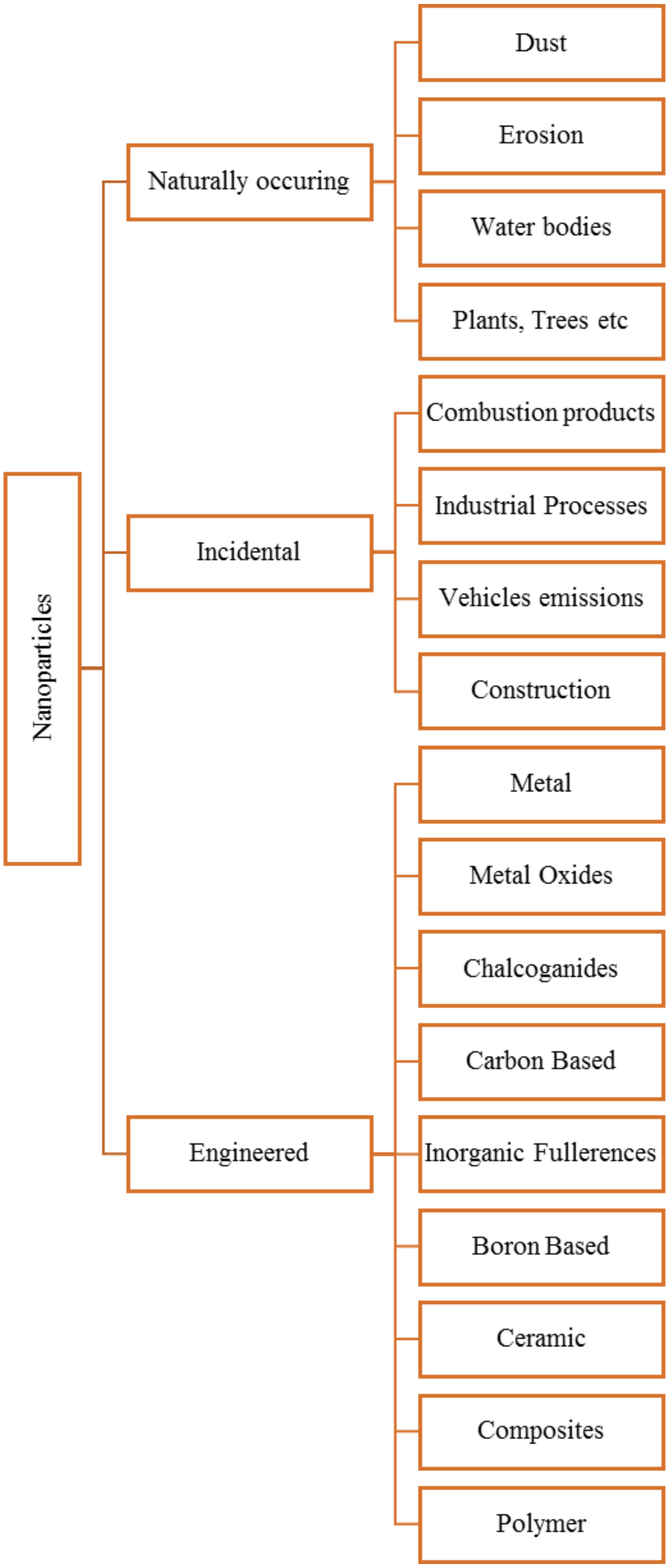


Fig. 2. Main classification of nanoparticles with subcategories of engineered nanoparticles in relevance to tribological studies.

The nanoparticles can be further subdivided on the basis of morphology, size and their source. In majority of research studies, researchers have synthesized the nanoparticles while many studies have also used commercially available nanoparticles. The morphology of nanoparticles is generally characterized by using Field Emission Scanning Electron Microscopy (FESEM) and High-resolution Transmission Electron Microscopy (HRTEM). **Fig. 3** shows the typical morphology characteristics using FESEM and HRTEM. **Table 1** shows the variation in these characteristics for nanoparticles which have been used in various studies.

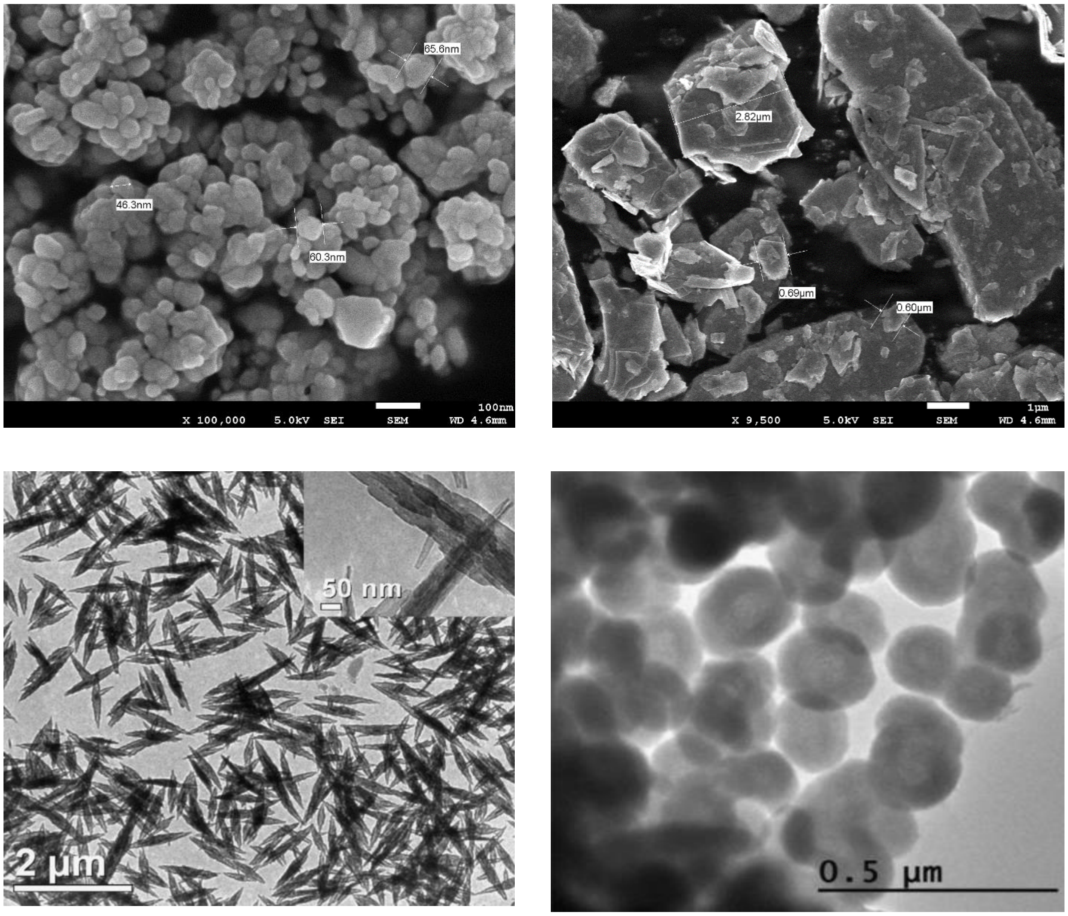


Fig. 3. Typical morphology of nanoparticles (a) FESEM for nanoCuO (Gulzar et al. 2015b) (b) FESEM of nanoMoS_2 (Gulzar et al. 2015b) (c) HRTEM for nanoCuO (Zhu et al. 2008) (d) HRTEM of nanoMoS_2 (Rabaso et al. 2014)

Type	Nanoparticle	Source	APS (nm)	Shape	Morphology Analysis Technique	References
Metal	Cu	Commercial	25	Nearly Spherical	TEM	(Viesca et al. 2011b)
	Ni	Commercial	20	Nearly spherical	TEM	(Chou et al. 2010)
	Al	Commercial	65	Spherical	SEM	(Peng et al. 2010b)
	Pb	Fabricated	2.2	Spherical	TEM	(Kolodziejczyk et al. 2007)
	Pb	Fabricated	40	Spherical	TEM, XRD	(Zhao et al. 2004)
Metal Oxides	CuO	Fabricated	5	Sphere-like	TEM	(Wu et al. 2007)
	CuO	Fabricated	4.35	Nearly spherical	SEM	(Alves et al. 2013)
	ZnO	Fabricated	11.71	Nearly spherical	SEM	(Alves et al. 2013)
	ZnO	Commercial	20	Nearly spherical	TEM	(Hernández Battez et al. 2007)
	TiO_2	Fabricated	80	Sphere-like	TEM	(Wu et al. 2007)
Chalcogenides	MoS_2	Commercial	90	Layered lamellar flaky	FESEM	(Koshy et al. 2015)
	MoS2	Fabricated	350,150	Layered	TEM	(Rabaso et al. 2014)
	MoS_2	Fabricated	100	Rectangular, oblate	SEM, TEM	(Yadgarov et al. 2013)
	WS_2	Fabricated	100	Spherical	AFM	(Rapoport et al. 2003)
	WS_2	Fabricated	120	Polyhedral, faceted	SEM, TEM	(Yadgarov et al. 2013)
Carbon based	Diamond	Commercial	10	Sphere-like	TEM	(Wu et al. 2007)
	Graphite	Commercial	55	Spherical	TEM	(Lee et al. 2009a)
	Carbon nanohorns	Commercial	80	Dahlia like	SEM	(Zin et al. 2015)
	Graphene	Fabricated	10	Spheroidal	TEM	(Joly-Pottuz et al. 2008)
Nitrides	BN	Commercial	70	Spherical	SEM	(Abdullah et al. 2016)
	BN	Commercial	114	Non-spherical	SEM, XRD	(Çelik et al. 2013)
Ceramic	Al_2O_3	Fabricated	78	Spherical	SEM	(Luo et al. 2014)
	SiO_2	Commercial	30	Spherical	FESEM, TEM	(Xie et al.

						2015)
	SiO_2	Fabricated	362, 215, 140, 58	Spherical	FESEM	(Peng et al. 2010a)
Composites	Al2O3/SiO2	Fabricated	70	Elliptical	TEM	(Jiao et al. 2011)
	ZrO2/SiO2	Fabricated	50-80	Nearly spherical	TEM	(Li et al. 2011)
Polymer	PTFE	Commercial	30-50	Spherical	FESEM	(Kumar Dubey et al. 2013)

Table 1 Summary of sources and typical properties of nanoparticles used as lubricant additives.

3. Role of Dispersion stability

When added to a fluid medium, nanoparticles sizes are small enough to remain dispersed in liquids by Brownian motion. First observed by Robert Brown and proven by Albert Einstein in 1905 (Einstein 1905), the it is the random motion of the particles. The particles in suspension may stick together and form bigger size agglomerates which may settle out due to gravity. The agglomeration of nanoparticles results in not only the sedimentation but also almost complete loss of antiwear or friction reduction. Therefore, dispersion stability is highly desirable for reliable lubrication performance and in this regard the main obstacle is the tendency of the nanoparticles to agglomerate (Tenne 2014). In case of poor dispersion stability, sedimentation and clogging may occur (Lee et al. 2009d). Stability means that the particles do not accumulate at a significant rate. **Fig. 4** shows two profiles for a dispersion of IF-MoS2 in a reciprocating test rig. Two cases of “stirred” and “not stirred” nanolubricant samples are considered showing loss of friction reduction of MoS2 nanoparticles.

As stable suspension is considered as a prerequisite of an effective nanolubricant formulation. The information of dispersion techniques and duration should be the essential part of such studies. There are various studies in the related literature with lack of information on the nanoparticles dispersion method (Chen and Liu 2006; Ma et al. 2010; Ye et al. 2003) and about stability of the nanolubricants (Hernández Battez et al. 2008b; Joly-Pottuz et al. 2008; Ma et al. 2010; Viesca et al. 2011a; Xie et al. 2015; Ye et al. 2003). In such studies, there is a high risk about the repeatability of reported results due to lack of significant information about dispersion technique, duration, the duration between preparation of suspension and tribological testing. As the suspension stability is vital issue that influences the nanolubricant lubrication performance, it is important to study and discuss the related influencing factors. This section will outline (a) methods of nanoparticles dispersion in lubricating oils, (b) dispersion stability analysis methods for nanolubricants, (c) methods to enhance the dispersion stability of nanolubricants.

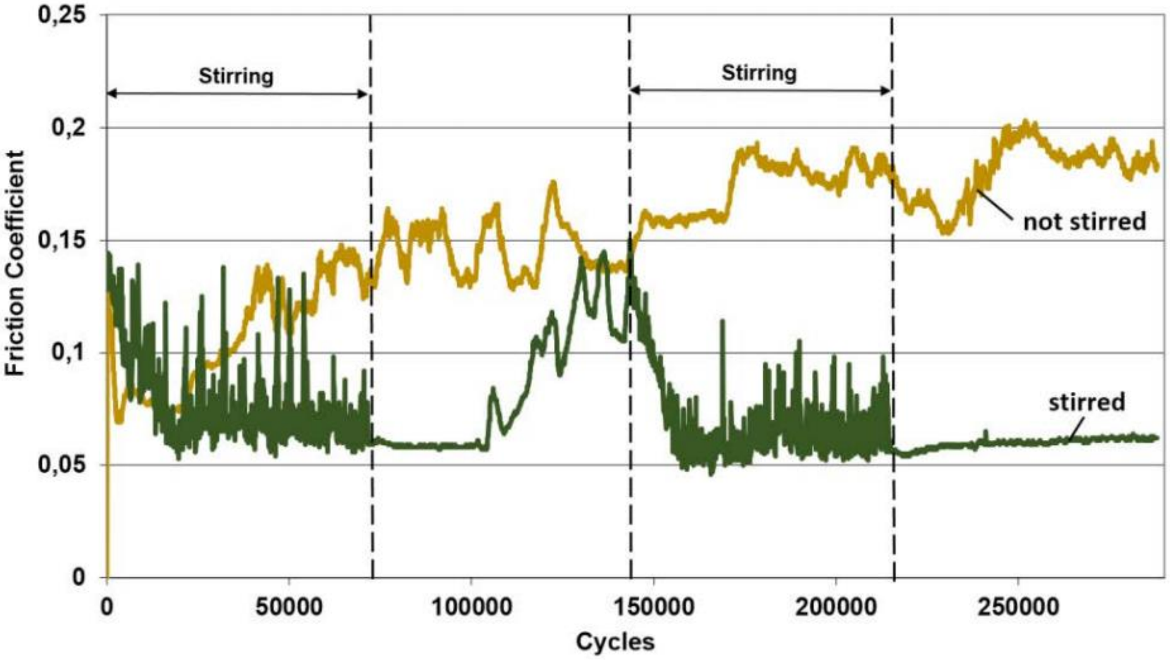


Fig.4 Friction behavior of “stirred” and “not stirred” lubricants showing effectiveness of stable dispersion for nanoMoS$_2$ enriched lubricant (Rabaso 2014).

3.1. *Methods of nanoparticles dispersion in lubricating oils*

For stable dispersion stability of nanolubricants, the selected method for dispersion is governing parameter after selection of lubricant and nanoparticles. According to P. Rabaso (Rabaso 2014) agitating the IF-MoS_2 enriched oil before testing helped reducing the size of agglomerates. Various methods have been used including magnetic stirring (Rabaso 2014), chemical agitation (Laad and Jatti 2016), agitation using ultrasonic shaker (Thottackkad et al. 2012; Xie et al. 2015), agitation using mechanical ball milling agitation and ultrasonic dispersion (Yu et al. 2008b) ultrasonic probe (Alves et al. 2013; Hernandez Battez et al. 2006; Hernández Battez et al. 2007; Hernández Battez et al. 2008b; Kumar Dubey et al. 2013; Pavlidou and Papaspyrides 2008; Viesca et al. 2011a; Viesca et al. 2011b; Yu et al. 2008a; Zhou et al. 2000) and ultrasonic bath (Asrul et al. 2013; Gulzar et al. 2015b; Hu et al. 2011; Joly-Pottuz et al. 2008).

After selection of dispersion method, the time duration of dispersion is also a key parameter to control the tendency of agglomerations. It has been observed that increasing mixing time leads to a decrease in the size of nanoparticles aggregates using ultrasonic bath (Joly-Pottuz et al. 2008). P. Rabaso (Rabaso 2014) has reported that the friction reduced significantly as the mixing time increased for IF-MoS_2 enriched oil. Thus agitation time duration plays an important role in dispersion stability and consequently affects the lubrication performance. Agitation duration of as low as only 2 minutes (Greco et al. 2011; Hernandez Battez et al. 2006; Hernández Battez et al. 2007; Hernández Battez et al. 2008a) and as high as 24 hours have been reported (Cho et al. 2012). **Table 2** shows commonly used dispersion methods and duration for different lubricants and nanoparticles combinations.

3.2. Dispersion stability analysis methods for nanolubricants

For investigation of dispersion stability, a number of different methods have been used. These methods include sedimentation, spectral absorbency, zeta potential and metallographic micrographs stability test. **Table 2** shows the commonly used methods in various research studies. The details of these stability investigation methods, procedures and limitations are given below.

3.2.1. Sedimentation method

Sedimentation is the simplest method to evaluate the stability of nanolubricants. This method has also been termed as "observation stability test" (Azman et al. 2016). For the stability evaluation, sedimentation photograph of samples in test tubes are usually taken (Amiruddin et al. 2015; Koshy et al. 2015; Kumar Dubey et al. 2013; Peng et al. 2010a; Peng et al. 2010b; Sui et al. 2015; Sui et al. 2016). The major disadvantage of this method is the long duration to acquire the results. In addition, precautions required same volume, temperatures and surrounding conditions for all the considered samples. This stability analysis is usually carried out immediately after the dispersion of nanoparticles in the lubricant. Disturbance or movements should also be avoided to ensure the reliability. **Fig. 5** shows the sedimentation of paraffin oil added with surface modified and unmodified aluminium nanoparticles which were recorder after 30 days from preparing.

The duration of this test varies from days to months. Peng et al. shows the sedimentation behavior after 30 days for silica and alumina nanoparticles dispersed in paraffin oil (Peng et al. 2010a; Peng et al. 2010b). In another study by T. Sui et al., the stability of the nano silica enriched PAO lubricants was studied by keeping the lubricants for 2 months (Sui et al. 2016). H. Amiruddin et al. evaluated the dispersion stability of SAE15W40 enriched with nanohBN for 60 days (Amiruddin et al. 2015). C.P. Koshy has mentioned a test duration of 100 days for coconut oil and paraffin oil enriched with nanoMoS_2 (Koshy et al. 2015). K. Dubey carried out this test for 7 days for PTFE based nanolubricants. Thus, different duration has been mentioned by researchers for different nanoparticles and lubricants combinations. Here it's worth mentioning that the key point for selection of test duration is based upon the observation of unusual dispersion behaviors of lubricant samples. Simply, the earlier the sediments are observed by naked eye, the test can be concluded.

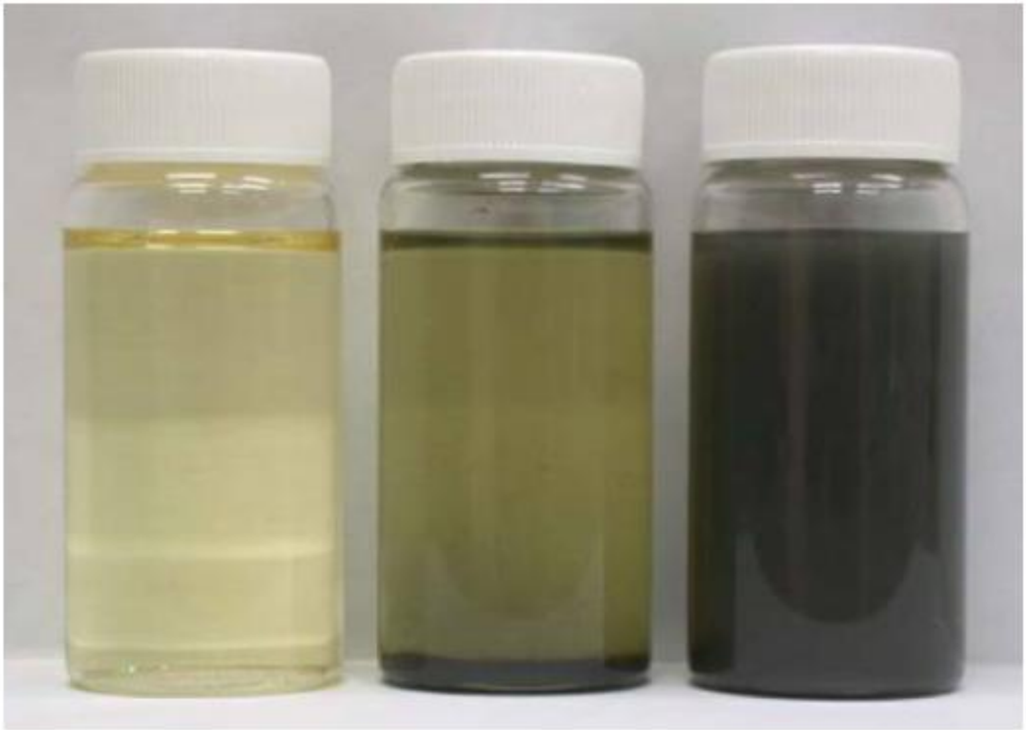


Fig. 5. Sedimentation of aluminium nanoparticles dispersed in paraffin oil (Peng et al. 2010b).

3.2.2. *Method of Spectral Absorbency*

Spectral absorbency is commonly used method to evaluate the stability of nanolubricants (**Table 2**). In this method, ultraviolet–visible (UV–vis) spectrophotometry absorbance measurements are used to characterize the colloidal stability of the dispersions. It is an easy and reliable method to evaluate the dispersion stability given that the nanomaterials dispersed in fluids have characteristic absorption bands in the wavelength range of 190–1100 nm (Yu and Xie 2012). In this method the lubricant samples are placed in quartz/glass cuvettes of typically 1 cm thickness and the absorption spectra are recorded on a spectrometer (Das et al. 2015). The advantage of this method comparing to other methods is to provide the quantitative concentration of nanolubricant samples (Yu and Xie 2012). This quantitative analysis provides a linear relation between the supernatant nanoparticle concentration and the absorbance. This method is also considered to be helpful in determining the sedimentation kinetics (Zhu et al. 2009). Like sedimentation method, different test duration has been mentioned by researchers for spectral absorbency analysis. Gulzar et al. carried out spectral absorbency analysis over a duration of 72 hours for biolubricant enriched with nanoCuO and nanoMoS2 (Gulzar et al. 2015b). Song et al. showed the absorbance profiles of lubricating oil enriched withnnanoZnAl2O4 for an analysis duration of 140 hours (Song et al. 2012). C.P. Koshy has mentioned a test duration of 120 hours for coconut oil and paraffin oil enriched with nanoMoS$_2$ (Koshy et al. 2015). V.S Jatti and T.P. Singh showed absorbance spectral behavior of nanoCuO enriched multi-grade engine oil over a time duration of 125 hours (Jatti and Singh 2015). Similarly, T. Luo et al. have shown optical absorbance for nanoAl2O3 enriched lubricating oil for 72 hours (**Fig. 6**) (Luo et al. 2014). From the analysis of various studies, it can be observed that the selection of test duration is based upon the observable variation in the absorbance behaviors of lubricant samples.

3.2.3. Zeta Potential Analysis

This method shows dispersion stability in terms of the potential difference between the dispersion medium and the stationary layer of fluid attached to the dispersed particle (Yu and Xie 2012). The absolute value of this parameter is used to illustrate the dispersion tendency of selected nanoparticles in lubricating oil. The higher the value of zeta potential (negative or positive), the better the electrical stability of dispersion. The low values of zeta potential show higher tendency of agglomeration or flocculation. In general, a value of 25mV (positive or negative) can be taken as reference value for deciding the suspension to be stable or not. As an example, Fig. shows trend of zeta potential values for nanoAl_2O_3 showing poor and better dispersion behaviors in the same lubricating oil.

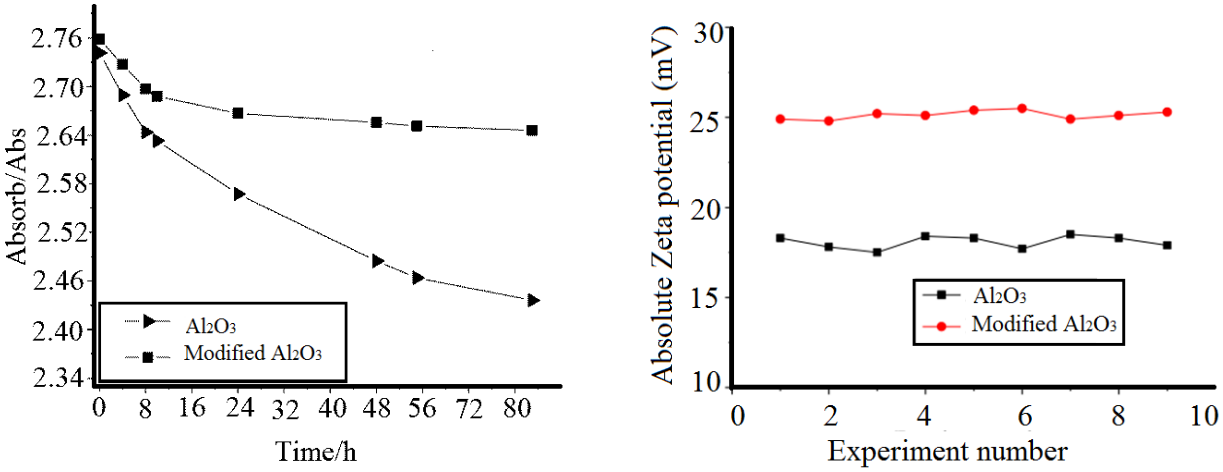


Fig. 6. Dispersion stabilty analysis showing comparison of poorly disperesd (Al_2O_3) and better dispersed nano-oils (Modified Al_2O_3) using (a) spectral absorbency (b) zeta potential (Luo et al. 2014).

3.2.4. Metallographic micrographs stability test

This method has been mentioned in very few studies (Azman et al. 2016; Singh and Suresh 2012). This method can be considered a variant of sedimentation method as the sediments and agglomeration are observed in single drop of nanolubricant by using microscope. As per procedure mentioned by S.S.N. Azman et al. (Azman et al. 2016), a drop of each sample is dropped on glass slide and left at room temperature. After few days, the samples are viewed using optical microscope to observe the agglomeration of nanoparticles in each sample. But the major disadvantage of this method is that the limitation of optical microscope to view up to nanometer scale. Additionally, there is no indication of time duration in the studies which have reported dispersion stability using this method (Azman et al. 2016; Singh and Suresh 2012). This is also the key issue in this method which means frequent microscopic observations are required to view the agglomeration.

3.3. ***Methods to enhance the dispersion stability of nanolubricants***

3.3.1. Nanoparticles surface modification

In this method, the surface properties of the nanoparticles are tailored by the organic modification agents. Commonly used modification agents like oleic acid is adsorbed around the nanoparticle, resulting in reducing their surface energy effectively to prevent the agglomeration (Peng et al. 2010a). The presence of organic chains enhances their dispersion stability in organic solvent. Studies have shown effectiveness of surface modification as mentioned in **Table 2**. In addition to organic acids (Chen and Liu 2006; Song et al. 2012; Ye et al. 2003), silane coupling agents (Jiao et al. 2011; Luo et al. 2014; Ma et al. 2010; Sui et al. 2015) are also found helpful in stable nanolubricant suspensions. As an example, the synthesis of amino silane surface modified nano silica is given in **Fig. 7.**

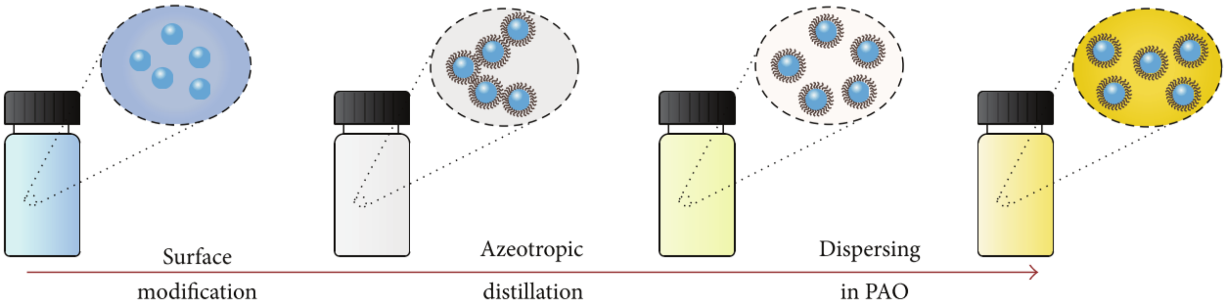


Fig.7. Schematics of synthesis and dispersion of surface modified hairy nano silica (Sui et al. 2015).

3.3.2. Effect of surfactant

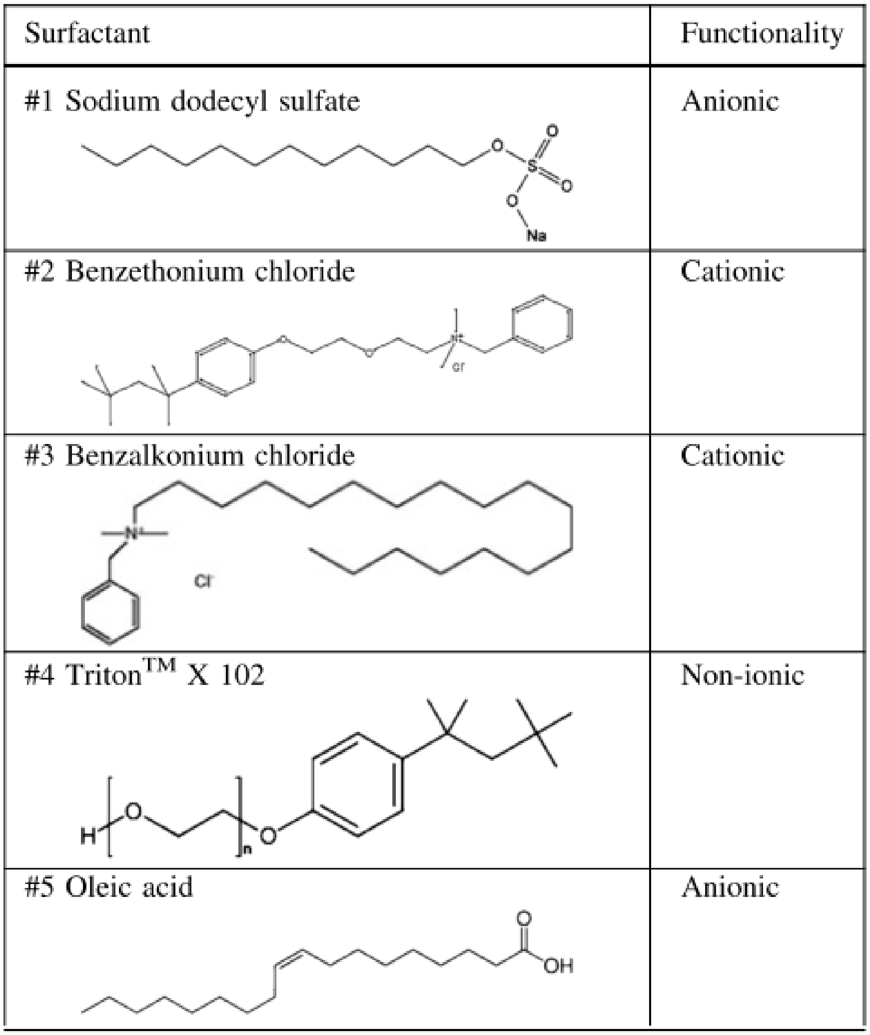
Surfactants used in nanolubricants are also termed as dispersants. Adding surfactants in the nanolubricants is an easy and economic method to enhance the dispersion stability. Commonly used surfactant include oleic acid (Abdullah et al. 2016; Demas et al. 2012; Gulzar et al. 2015a; Gulzar et al. 2015b) and sodium dodecyl sulfate (SDS) (Demas et al. 2012; Koshy et al. 2015). N.G Demas et al. (Demas et al. 2012) have studied five different surfactants to evaluate the dispersion of nanoMoS2 and nanoBN in PAO. They reported that the use of surfactant was not only beneficial in suspending the nanoparticles, but also reduced the friction and wear by itself. **Table 3** shows the structure and functionality of few surfactants.

Table 2 Literature summary of commonly used dispersion methods, duration, techniques to improve dispersion stability and dispersion stability measuring methods.

Particle	Lubricant	Dispersion Method and Duration	Surface Modification	Surface Modifying Agent/ Surfactant	Effect on dispersion	Dispersion Stability Test	Ref
ZrO_2/SiO_2	$20^{\#}$ Machine Oil	Ultrasonic dispersion 30 min	Yes	aluminum zirconium coupling agent	Positive	Zeta Potential, UV-Vis Absorbance	(Li et al. 2011)
Al_2O_3/SiO_2	$20^{\#}$ Machine Oil	Ultrasonic dispersion 30 min	Yes	Silane coupling agent KH-560	Positive	Sedimentation	(Jiao et al. 2011)
Al_2O_3	$20^{\#}$ Machine Oil	ultrasonic dispersion, 30 min	Yes	Silane coupling agent KH-560	Positive	Sedimentation ,Zeta potential UV-Vis Absorbance	(Luo et al. 2014)
TiO_2	Servo 4T Synth 10W-30	chemical shaker for agitation, 30 min	No	-	-	UV-Vis Absorbance	(Laad and Jatti 2016)
$ZnAl_2O_4$	Lubricating Oil	-	Yes	Oleic acid	Positive	UV-Vis Absorbance	(Song et al. 2012)
CuO	Multi-grade engine oil	ultrasonic agitation ,30 minutes	No	-	-	UV-Vis Absorbance	(Jatti and Singh 2015)
TiO_2	Liquid Paraffin		Yes	Tetrafluorobenzoic acid	Not Given	No	(Ye et al. 2003)
ZrO_2	20# machine oil		Yes	Silane coupling agent KH-560	Not Given	No	(Ma et al. 2010)
CuO	Mineral, PAO, Vegetable	ultrasonic probe, 30 min	No	-	-	No	(Alves et al. 2013)
ZnO	Mineral, PAO, Vegetable	ultrasonic probe, 30 min	No	-	-	No	(Alves et al. 2013)
ZnO	60SN base oil	ultrasonic bath 30 minutes, stirrer 20 minutes	Yes	Oleic acid	Improved	Sedimentation	(Ran et al. 2016)
CuO	Palm TMP ester	ultrasonic bath, 2 h	Yes	Oleic acid	Improved	UV-Vis Absorbance	(Gulzar et al. 2015b)
MoS_2	Palm TMP ester	ultrasonic bath, 2 h	Yes	Oleic acid	Improved	UV-Vis Absorbance	(Gulzar et al. 2015b)
CuO	SAE-40, Coconut oil	ultrasonic shaker, 40 minutes	No	-	-	UV-Vis Absorbance	(Thottackkad et al. 2012)
MoS_2	Coconut oil	ultrasonic shaker for 60 min with intermittent stopping for 3min	Yes	sodium dodecyl sulfate (SDS)	Improved	UV visible spectroscopy	(Koshy et al. 2015)
MoS_2	Mineral oil	ultrasonic shaker for 60 min with intermittent stopping for 3min	Yes	sodium dodecyl sulfate (SDS)	Improved	UV visible spectroscopy	(Koshy et al. 2015)
SiO_2	liquid paraffin	ultrasonic stirrer, 60 min	Yes	Oleic acid	Improved	Sedimentation	(Peng et al. 2010a)
PbS	liquid paraffin	Not given	Yes	Oleic acid	Improved	No	(Chen and Liu 2006)
hBN	SAE 15W-40	ultrasonic homogenizer, 20 min	Yes	Oleic acid	Improved	No	(Abdullah et al. 2016)
hairy silica	PAO100	Stirrer	Yes	Amino Functionalized	Improved	Sedimentation	(Sui et al. 2015)
Cu	PAO6	ultrasonic probe, 30 min	No	-	-	Sedimentation	(Viesca et al. 2011a)
Cu Carbon	PAO6	ultrasonic probe, 30 min	No	-	-	Sedimentation	(Viesca et al. 2011a)

Coated							
Carbon nano-onions	PAO	Ultrasonic bath, 300 min	No	-	-	Sedimentation	(Joly-Pottuz et al. 2008)
Ni	PAO6	ultrasonic probe, 30 min	No	-	-	Sedimentation	(Chou et al. 2010)
ZrO_2	PAO6	ultrasonic probe, 2 min	No	-	-	Sedimentation	(Hernández Battez et al. 2008b)
Carbon onion, Graphite	sPAO	ultrasonic bath, 300 min	No	-	-	No	(Joly-Pottuz et al. 2008)
ZnO	PAO6	ultrasonic probe, 2 min	No	-	-	No	(Hernández Battez et al. 2008b)
SiO_2	EOT5#	ultrasonic shaker, 120 min	No	-	-	No	(Xie et al. 2015)
MoS_2	EOT5#	ultrasonic shaker, 120 min	No	-	-	No	(Xie et al. 2015)

Table 3 Typical surfactants, their chemical structure and functionality (Demas et al. 2012).



Surfactant	Functionality
#1 Sodium dodecyl sulfate	Anionic
#2 Benzethonium chloride	Cationic
#3 Benzalkonium chloride	Cationic
#4 Triton^{TM} X 102	Non-ionic
#5 Oleic acid	Anionic

4. Role of Nanoparticle Concentration

Suitable concentration is another important factor which affects the lubrication characteristics of nanolubricants (Koshy et al. 2015; Luo et al. 2014; Sui et al. 2015; Thottackkad et al. 2012). Addition of nanoparticles, either too little or too much, might causes harmful effects in some cases either by increasing friction or wear (Azman et al. 2016). A suitable concentration of nanoparticles is required to improve the friction and wear behavior (**Table 4**). The path to suitable nanoparticle concertation for a lubricating oil depends upon three crucial factors which include dispersion method/time, role of nanoparticle (friction modifier/antiwear/EP additive) and tribo-test conditions. **Table 4** shows summary of literature showing range of concentrations and optimum concentrations along with role of nano-additive for different lubricants and nanoparticles combinations. It is interesting to observe that same MoS_2 nanoparticles show different optimum concentration for two different lubricants i.e. 0.58 wt% for mineral oil and 0.53 wt% for coconut oil using pin on disk contact (Koshy et al. 2015). Contradictory to it, a fixed optimum concentration of 0.5 wt% nanoCuO and nanoZnO has been used for mineral, synthetic and vegetable oils for ball on disk contact (Alves et al. 2013). It shows that the optimum concentration is strongly system specific which means it will vary for each test condition.

Table 4 Literature summary of role of nanoparticles and optimum concentrations for different lubricating oils.

Particle	Lubricant	Nanoparticle Role	Conc. (wt%)	Optimum Conc. (wt%)	Ref
ZnO	Mineral, PAO, Sunflower, Soybean	Friction Modifier, Antiwear	0.5	0.5	(Alves et al. 2013)
ZnO	60SN base oil	Friction Modifier, Antiwear	0.5	0.5	(Ran et al. 2016)
CuO	Palm TMP ester	Antiwear, EP	1	1	(Gulzar et al. 2015b)
MoS_2	Palm TMP ester	Antiwear, EP	1	1	(Gulzar et al. 2015b)
CuO	Coconut oil	Friction Modifier, Antiwear	0.1-0.6	0.34	(Thottackkad et al. 2012)
MoS_2	Coconut oil	Friction Modifier, Antiwear	0.25,0.5,0.75,1	0.53%	(Koshy et al. 2015)
MoS_2	Mineral oil	Friction Modifier, Antiwear	0.25,0.5,0.75,1	0.58%	(Koshy et al. 2015)
SiO_2	liquid paraffin	Friction Modifier, Antiwear	0.0125, 0.025, 0.05,0.1,0.2,0.5, 1, 2, 4	0.05-0.5wt%	(Peng et al. 2010a)
PbS	liquid paraffin	Friction Modifier, Antiwear	0.05-0.2	0.2	(Chen and Liu 2006)
Fe_3O_4	$^{\#}$40 engine oil	Friction Modifier, Antiwear	0.5, 1.0, 1.5, 2.0	1.5	(Gao et al. 2013)
hairy silica	PAO100	Friction Modifier, Antiwear	0.5,1,2,4	1	(Sui et al. 2015)
Cu	PAO6	Antiwear, EP	0.5,2	0.5	(Viesca et al. 2011a)
Cu Carbon Coated	PAO6	Antiwear, EP	0.5,2	0.5	(Viesca et al. 2011a)
Carbon nano-onions	PAO	Friction Modifier, Antiwear	0.1	0.1	(Joly-Pottuz et al. 2008)
Ni	PAO6	Friction Modifier, Antiwear, EP	0.5, 1 and 2	0.5	(Chou et al. 2010)
CuO	chemically modified rapeseed oil	Friction Modifier, Antiwear	0.1,0.5,1	0.5	(Arumugam and Sriram 2014)
ZrO2	PAO6	Antiwear, EP	0.5%, 1.0% and	0.5	(Hernández Battez

			2.0%		et al. 2008b)
ZnO	PAO6	Antiwear, EP	0.5%, 1.0% and 2.0%	0.5	(Hernández Battez et al. 2008b)
CuO	PAO6	Antiwear, EP	0.5%, 1.0% and 2.0%	0.5	(Hernández Battez et al. 2008b)
SiO_2	EOT5#	Friction Modifier, Antiwear, EP	0.2, 0.5, 0.7 and 1.0	0.7	(Xie et al. 2015)
MoS_2	EOT5#	Friction Modifier, Antiwear, EP	0.2, 0.5, 0.7 and 1.0	1	(Xie et al. 2015)
MoS_2	(SE 15W-40, Sinopec Lubricants, China)	Friction Modifier, Antiwear, EP	0.1, 0.5, 1.0, 2.0 and 5.0	~ 1	(Wan et al. 2014)
ZrO_2/SiO_2	$20^{\#}$ Machine Oil	Friction Modifier, Antiwear	0.05, 0.1, 0.3, 0.5, 0.75,1	0.1	(Li et al. 2011)
$Al2O_3/SiO_2$	$20^{\#}$ Machine Oil	Friction Modifier, Antiwear	.05, 0.1 0.5,1	0.5	(Jiao et al. 2011)
Al_2O_3	$20^{\#}$ Machine Oil	Friction Modifier, Antiwear	.05, 0.1 0.5,1	0.1	(Luo et al. 2014)
TiO_2	Servo 4T Synth 10W-30	Friction Modifier, Antiwear	0.3,0.4,0.5	0.3	(Laad and Jatti 2016)
$ZnAl_2O_4$	Lubricating Oil	Friction Modifier, Antiwear	0.05, 0.1, 0.5, 1	0.1	(Song et al. 2012)
CuO	Mineral based multi-grade engine oil	Friction Modifier, Antiwear	0.5, 1, 1.5	1.5	(Jatti and Singh 2015)
CuO	SAE 75W-85	Friction Modifier, Antiwear, EP	0.5, 1.0, and 2.0	2	(Peña-Parás et al. 2015)
CuO	PAO 8	Friction Modifier, Antiwear, EP	0.5, 1.0, and 2.0	2	(Peña-Parás et al. 2015)
ZrO_2	20# machine oil	Friction Modifier, Antiwear	0.1,0.5,1	0.5	(Ma et al. 2010)
CuO	Mineral, PAO, Sunflower, Soybean	Friction Modifier, Antiwear	0.5	0.5	(Alves et al. 2013)

5. Role of Nanoparticle size

The tribological performance of a nanolubricants has a direct linkage to the nanoparticle size in a number of ways. Firstly, the dispersion stability is a function of nanoparticle size which is a major requirement for proper nanolubricant formulation. In this regard, the sedimentation rate is an important parameter to determine the dispersion stability which can be calculated using Stokes' law

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

v_z is settling velocity, ρ_{NP} is density of nanoparticle and ρ_F is density of fluid, g is gravity, r is the radius of nanoparticle, and μ is the viscosity of the fluid. This simple equation shows that for 10-fold increase in nanoparticle size (e.g., 100 nm instead of 10nm), sedimentation time will decrease 100-fold. It shows role of nanoparticle size in achieving stable nanolubricant.

Secondly, the small size of nanoparticles helps them to penetrate the rubbing surfaces and their reaction with environment depend upon their surface-to-volume ratio. The intrinsic mechanical properties like hardness is determined by its size which in turn effect the tribological behavior. For materials in the size range of 100 nm or greater the hardness increases with shrinking particle size (Schiøtz and Jacobsen 2003; Weertman 1993). If the hardness of nanoparticles is higher than the hardness of material of tribo-pair, the result is indentation and scratching. Same phenomenon has been reported by L. Peña-Parás et al. (Peña-Parás et al. 2015). According to their study, high hardness (8–9 Mohs) of nanoAl_2O_3 than the metal substrate resulted in abrasive wear and nanoparticle re-agglomeration. Therefore, the relationship between size and hardness of nanoparticles must be taken care of while formulating nanolubricant.

Lastly, while considering the suitable nanoparticle size selection, the ratio of root mean square roughness of lubricated surface to the radius of nanoparticle is an important parameter. If the nanoparticles size is too big as compared to gap between asperities, they will not deposit on the contact zone which lead to poor lubrication.

6. Role of nanoparticle shape and structure

For various type of tribological applications, the role of nanoparticle shape plays an important role. The shape of nanoparticle corresponds to pressure experienced by nanoparticles upon loading. Spherical shape nanoparticles show high load carrying capacity and extreme pressure characteristics due to their ball bearing effect (Luo et al. 2014). The reason for this behavior is based upon the contact between nanoparticle and the lubricated surface. Spherical shape of nanoparticles results in point contact with the counter surface. The line contact is resulted by nanosheets while planar contact is the feature of nanoplatelets (**Fig. 8**). Thus the shape of nanoparticle can be selected on the basis of contact pressures between interacting surfaces. In majority of studies related to use of nanolubricants, spherical shape nanoparticles have been used (Joly-Pottuz et al. 2008; Kolodziejczyk et al. 2007; Lee et al. 2009a; Luo et al. 2014; Peng et al. 2010a; Peng et al. 2010b; Rapoport et al. 2003). The commonly used shapes of nanoparticles are listed in **Table 1**.

While characterizing the morphology of nanoparticles, their internal nanostructure can influence their tribological properties. Commonly used nanoparticle, such as graphite, h-BN, and transition metal dichalcogenides, owe their lubrication performance to a layered structure (Demas et al. 2012). **Fig. 9** shows the molecular structure of MoS_2 as an example of layered crystal structure. In comparison to the typical transition metal dichalcogenides, fullerene-like nanoparticles (IF) have been developed which are layered compounds with a hollow polyhedral structure (Tevet et al. 2011). They have shown superior tribological behavior for severe contact conditions, and have tendency to form tribo-films on interacting surfaces through the exfoliation of their outer nano-layers (Gullac and Akalin 2010; Rabaso 2014). Such IF solid nanoparticles can engage additional lubrication mechanisms of "exfoliation" as shown in **Fig 10.**

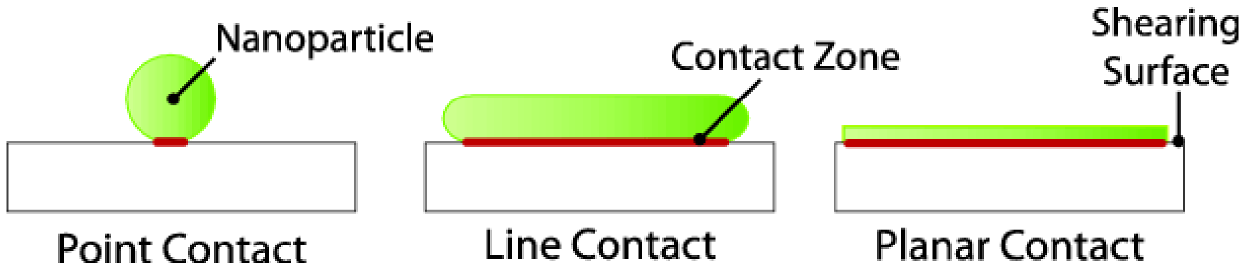


Fig. 8. The effect of nanoparticle shape on the contact pressures upon loading (Akbulut 2012).

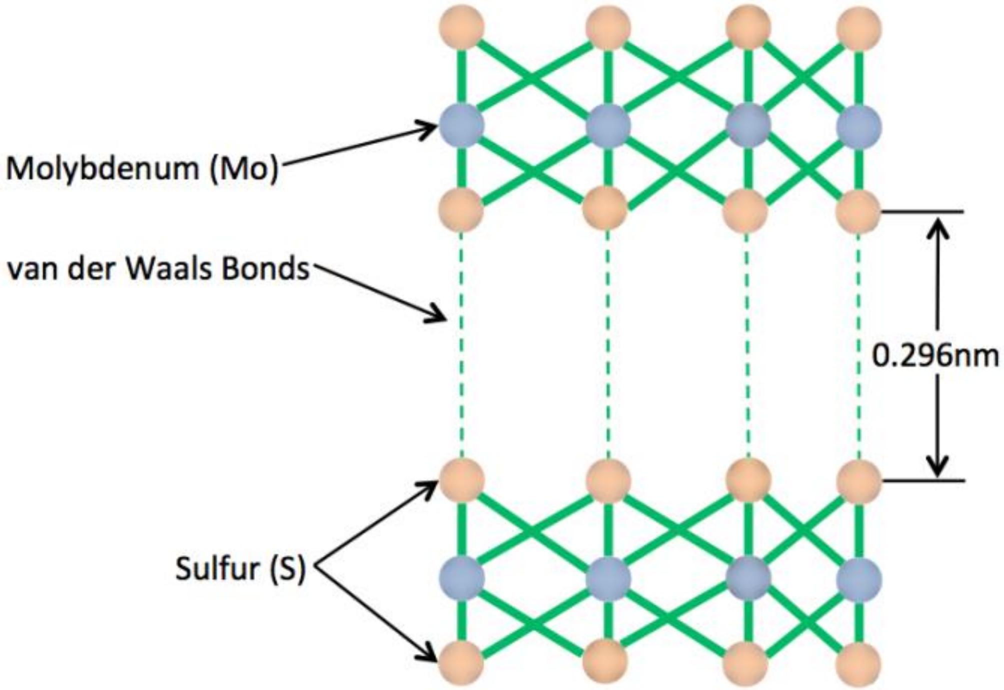


Fig. 9. Illustration of the layered crystal molecular structure of MoS_2 (Reeves 2013).

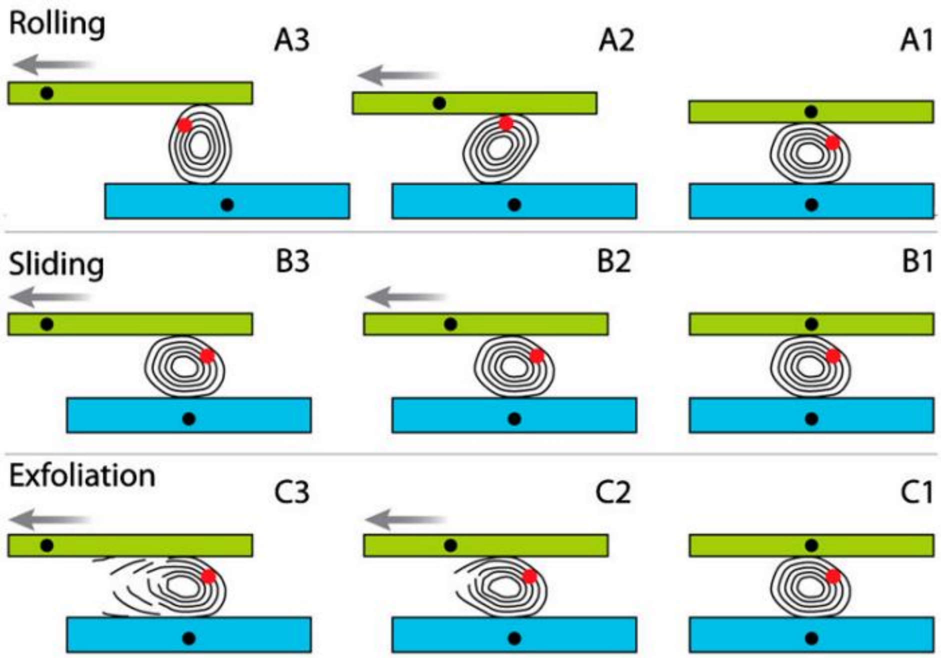


Fig. 10. Main friction mechanisms of multilayered IF nanoparticles: rolling (A), sliding (B), and exfoliation (C) (Tevet et al. 2011).

7. Role of Tribo-Testing Conditions

Unlike dissolved additives, for nanoparticles the rubbing surfaces enhancement is also strongly dependent on the mechanics of the rubbing contact and the presence of separating oil films (Spikes 2015). M.R. Falvo and R. Superfine (Falvo and Superfine 2000) have shown that the relative orientation of the interacting surfaces affects the frictional behavior for nanometer scale lubrication system. This means that tribological effectiveness of nanolubricants is likely to be very system-specific and as a result, very different performance is likely to be observed in different test conditions.

To investigate the tribological performance of nanoparticles as additives in lubricating oils, various experimental studies were carried out using different geometric configurations, which include four-ball, ball-on-flat, pin-on-disk, cylinder-on-flat, piston ring on cylinder liner and block on ring (**Fig. 11**). Most of the studies were conducted at a normal operating temperature of an engine (i.e., 70–100 C) as mentioned in **Table 5** and **Table 6**. Similarly, values of other test parameters, such as normal load, sliding distance, sliding velocity, and test duration also varied. For extreme pressure characteristics and load carrying ability of nanolubricants, majority of nanolubricants have been tested for four-ball test geometry using ASTM D2783 standard conditions (Abdullah et al. 2016; Chou et al. 2010; Gulzar et al. 2015b; Hernández Battez et al. 2008b; Viesca et al. 2011b). Therefore, **Table 5** shows the summary of only four-ball test conditions by different researchers. For friction behavior and antiwear characteristics, most of the researchers used sliding contact while simulating contact between different counter bodies. **Table 6** shows the test conditions for various type of geometric configurations other than four-ball test geometry.

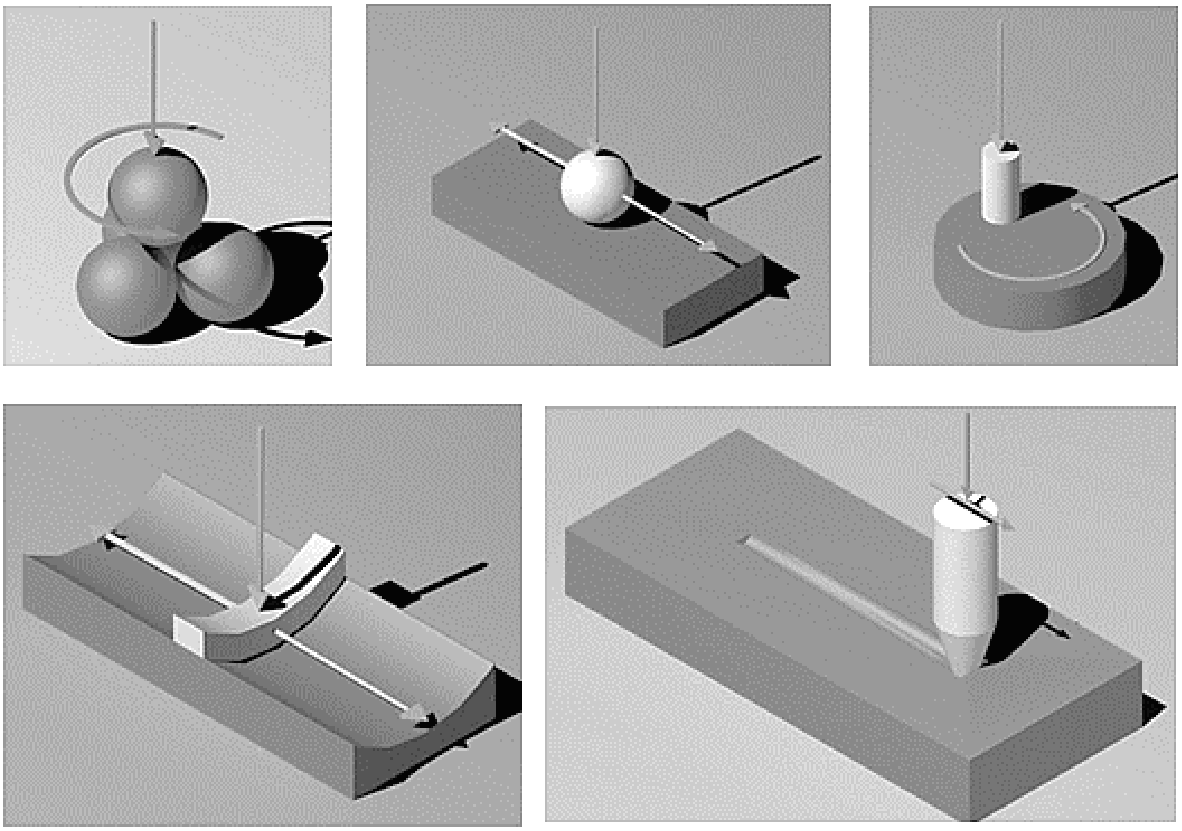


Fig. 11. Commonly used tribo-testing geometric configurations (a) four-ball, (b) ball-on-flat, (c) pin-on-disk (d) piston ring-cylinder (e) pin -on-flat.

Table 5 Literature summary of four-ball test conditions.

Nanoparticle	Lubricant	Test Duration (sec)	Temp ◦C	Normal Load (N)	Speed rpm	Output Parameters	References
ZnO	PAO6	3600	75	392	1200	WSD	(Hernandez Battez et al. 2006)
ZnO	60SN base oil	1800	75	500	1000	WSD, Friction	(Ran et al. 2016)
$CaCO_3$	PAO+5% Chemically modified palm oil	3600	25	392	1200	WSD, Friction	(Zainal et al. 2015)
MoS_2	SAE 20W-40	3600	75	392	600, 1200	WL, WSD	(Thakur et al. 2016)
Al_2O_3/SiO_2	$20^{\#}$ Machine Oil	1800	75	147	1,450	Friction, WSD	(Jiao et al. 2011)
CuO, ZnO, ZrO_2	PAO6	10 /stage till weld	25	Varies/stage till weld	1470	ISL, LNSL, WL, LWI, WSD	(Hernández Battez et al. 2008b)
PTFE	150N Group II base oil	3600	75	392	1200	WL, WSD	(Kumar Dubey et al. 2013)
MoS_2	SAE 20W-40	10 /stage till weld	25	Varies/stage till weld	1470	ISL, WL, LWI, WSD	(Thakur et al. 2016)
ZrO_2/SiO_2	$20^{\#}$ Machine Oil	1800	75	147	1,450	Friction, WSD	(Li et al. 2011)
Ni	PAO6	10 /stage till weld	25	Varies/stage till weld	1470	ISL, LNSL, WL, LWI, WSD	(Chou et al. 2010)
hBN	SAE 15W-40	10 /stage till weld	25	Varies/stage till weld	1760	WSD	(Abdullah et al. 2016)
MoS_2/TiO_2	liquid paraffin	1800	25	300	1450	WSD, Friction	(Hu et al. 2011)
Cu	PAO6	10 /stage till weld	25	Varies/stage till weld	1470	ISL, WL, LWI, WSD	(Viesca et al. 2011b)
CuO	liquid paraffin	900	60-70	392	1200	WSD, Friction	(Asrul et al. 2013)
CuO	PAO6	10 /stage till weld	25	Varies/stage till weld	1470	Friction, ISL, LNSL, WL, LWI, WSD	(Fernandez et al. 2008)
CuO, MoS_2	Chemically modified palm oil	10 /stage till weld	25	Varies/stage till weld	1770	ISL, LNSL, WL, LWI, WSD	(Gulzar et al. 2015b)
Al_2O_3/SiO_2	$20^{\#}$ Machine Oil	1800	75	147	1,450	Friction, WSD	(Jiao et al. 2011)
Fe, Cu, Co	SAE10	3600	25	150	1420	WSD, Friction Torque	(Padgurskas et al. 2013)
WS_2	Chemically modified jatropha oil	10 /stage till weld	25	Varies/stage till weld	1770	ISL, LNSL, WL, LWI, WSD	(Gulzar et al. 2015a)
TiO_2	Chemically modified palm oil	300	25	392,784,1176, 1568	1200	WSD, Friction	(Zulkifli et al. 2013)
ZnO	PAO6	10 /stage till weld	25	Varies/stage till weld	1470	ISL, LNSL, WL, LWI, WSD	(Hernandez Battez et al. 2006)
Cu	liquid paraffin	1800	-	300	1450	WSD, Friction	(Zhang et al. 2015)

Table 6 Literature summary of tribo-test conditions simulating different counter-bodies

Nanoparticle	Lubricant	Geometric Configuration	Contact	Test Duration (sec)	Temp	Normal Load (N)	Contact Pressure (Gpa)	Speed	References
Cu	PAO6	block-on-ring	Sliding	3066	-	165	0.1	1 (m/s)	(Viesca et al. 2011b)
MoS_2, BN	PAO10	Piston skirt-cylinder liner	Sliding	10800	20,40,100	250	-	120 (rpm)	(Demas et al. 2012)
CuO	Chemically modified rapeseed oil	Piston ring-cylinder liner	Sliding	7200	60	80	0.005	600 (rpm)	(Arumugam and Sriram 2014)
CuO	Mineral oil	Pin-on-disk	Sliding	400,600, 1200	-	40,60	-	0.5 , 1.0, 1.5 (m/s)	(Jatti and Singh 2015)
WS_2	SAE 30	Piston ring-cylinder liner	Sliding	27000	70	160	0.01	2.29 (m/s)	(Gullac and Akalin 2010)
WS_2	Paraffin oil	Pin-on-disk	Sliding	24000	-	100–500	-	0.6 (m/s)	(Rapoport et al. 2003)
C60	Mineral oil	disk-on-disk	Rotating	600	26-28	1000-1500	-	1000 (rpm)	(Cho et al. 2012)
Pb	Paraffin oil	pin-on-disk	Sliding	5000	-	7	1.26	1 (m/s)	(Kolodziejczyk et al. 2007)
CuO, MoS_2	Chemically modified palm oil	Piston ring-cylinder liner	Sliding	21600	70	160	0.01	1.1 (m/s)	(Gulzar et al. 2015b)
Cu, TiO2, Carbon horns	SAE40	ball-on-flat	Sliding	120 /step for 13 steps	25	-	0.6	0.001–1.8 m/s	(Zin et al. 2015)
CuO, ZnO, ZrO_2	PAO6	block-on-ring	Sliding	1533	-	165	0.1	2 (m/s)	(Hernández Battez et al. 2008b)
Ni	PAO6	block-on-ring	Sliding	1533	-	165	0.1	2 (m/s)	(Chou et al. 2010)
BN	SAE10W	Ball on disk	Sliding	160	20	10	2.93	0.25 (m/s)	(Çelik et al. 2013)
Graphite	Vegetable based oil	pin-on-disk	Sliding	3600	24	2,10	-	100 (rpm)	(Su et al. 2015)
Carbon Nano-onions, Graphite	PAO	pin-on-flat	Sliding	1000, 20000	25	2,5,10	0.83,1.12,1.42	0.25 (m/s)	(Joly-Pottuz et al. 2008)
MoS_2, SiO_2	EOT5# engine oil	ball-on-flat	sliding	1800, 4500	25	1,3,5,8	0.223, 0.312, 0.381, 0.446	0.08,0.03 (m/s)	(Xie et al. 2015)
Graphite	commercial mineral oil, Supergear EP220	disk-on-disk	rotating	600	35	500,1000, 1500,2000, 2500,3000	-	1000 (rpm)	(Lee et al. 2009a)
BN	SE 15W-40	disk-on-disk	rotating	180	25	500	-	500rpm	(Wan et al. 2015)
MoS_2	PAO 4 + PAO 40	ball-on-flat	sliding	144000 cycles	80	10	1.4	600 (rpm)	(Rabaso et al. 2014)
CuO	Coconut Oil	pin-on-disc	sliding	178 to 714	-	49 to 98	0.001 to 0.002	1.4 to 5.6 (m/s)	(Thottackkad et al. 2012)
CuO, Al_2O_3	PAO8, SAE 75W-85)	Ball on disk	Sliding	7200	50	200	-	3000 (rpm)	(Peña-Parás et al. 2015)
CuO	Mineral, PAO, Sunflower, Soybean	ball-on-disk	Sliding	3600	50	10	-	1200 (rpm)	(Alves et al. 2013)
ZrO_2/SiO_2	$20^{\#}$ Machine Oil	Thrust ring	Rubbing	1800	75	200	-	1,200 (rpm)	(Li et al. 2011)
Al_2O_3/SiO_2	$20^{\#}$ Machine Oil	Thrust ring	Rubbing	1800	75	200	-	1,200 (rpm)	(Jiao et al. 2011)

8. Lubrication Mechanisms

The investigation of lubrication mechanisms is considered as a crucial parameter to completely understand the tribology of nanoparticles. However, defining the active mechanisms remained a subject of debate for many research studies related to nanoparticles based lubrication systems. A number of mechanisms have been proposed by researchers using the surface analysis techniques to explain the lubrication enhancement of the nanoparticle-suspended lubricating oil. These mechanisms include the ball bearing effect (Chiñas-Castillo and Spikes 2003; Rapoport et al. 2002; Wu et al. 2007), protective film (Ginzburg et al. 2002; Hu et al. 2002; Xiaodong et al. 2007), mending effect (Liu et al. 2004) and polishing effect (Tao et al. 1996). T.Sui et al. (Sui et al. 2015) reported all these lubrication mechanisms for PAO enriched with amino functionalized hairy silica nanoparticles (**Fig.12**)

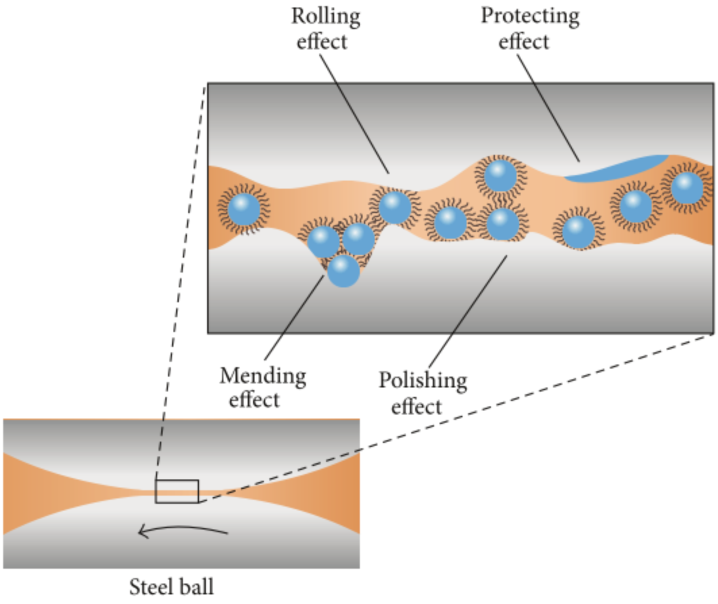


Fig. 12. Schematic diagram of the lubrication mechanism of silica nanoparticle dispersed in PAO (Sui et al. 2015).

These mechanisms can be categorized into two main groups. The first is the direct effect of the nanoparticles which includes ball bearings effect and protective/tribo-film formation. The other is the secondary effect which contributes in surface enhancement by mending/repairing effect and polishing/smoothing effect. **Table 7** shows literature summary of majorly reported lubrication mechanisms for different nanoparticles/lubricating oils combinations.

For better understanding, detail of potential lubrication mechanisms by presence of nanoparticles, are given below.

8.1. Ball bearing effect

The spherical and quasi spherical nanoparticles believed to function like tiny ball bearings which roll into the contact area. Small spherical as well as quasi spherical nanoparticles are more likely to roll between the shearing surfaces and change the sliding friction for a mixing of sliding and rolling friction. This lubrication mechanism is attributed to tribo-pair system having stable low-load conditions between the shearing surfaces to maintain the shape and rigidity of the nanoparticles. **Fig. 13.** illustrates the ball bearing mechanism. This mechanism of tested surfaces protection has been reported by a number of researchers (**Table 7**).

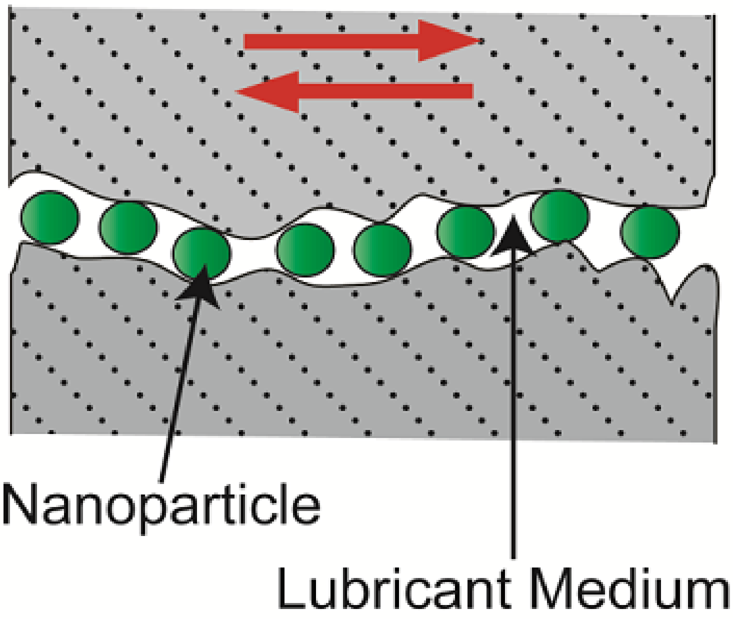


Fig. 13. Illustration of ball bearing mechanism by nanoparticles based lubrication (Kheireddin 2013).

8.2. Protective film formation

Protective film on the tested surfaces is also referred as tribo-film. Tribo-films and near-surface materials govern the tribological behaviors of interacting surfaces. This film formation is triggered by the reaction between the treated material and the additives under the provided environment (Gulzar et al. 2015b) or tribo-sintered (Chou et al. 2010; Viesca et al. 2011b). There are many rather majority of experimental studies which have reported tribo-film formation mechanism for superior lubrication (**Table 7**). A. Verma et al. (Verma et al. 2008) reported the formation a durable tribo-film with the Mo, S, and P elements, reducing the chances of severe wear, friction, and seizure for nnaoMoS_2 based lubricant. There are a number of studies which show friction as well as wear reduction by this mechanism of protective film formation (Demas et al. 2012; Rapoport et al. 2003). However, in experimental study using CeF_3 based nanolubricant, poor anti-wear behavior has been observed due to corrosion from

F- surface atoms (Sunqing et al. 1999). **Fig.14** shows the schematics of tribo-film formation which is not only providing the surface protection but also help to protect material from crack propagation by reducing friction between asperities. The formation of this tribo-film is generally verified by using analysis techniques like SEM/EDS, Raman spectroscopy and XPS as given in **Table 7**.

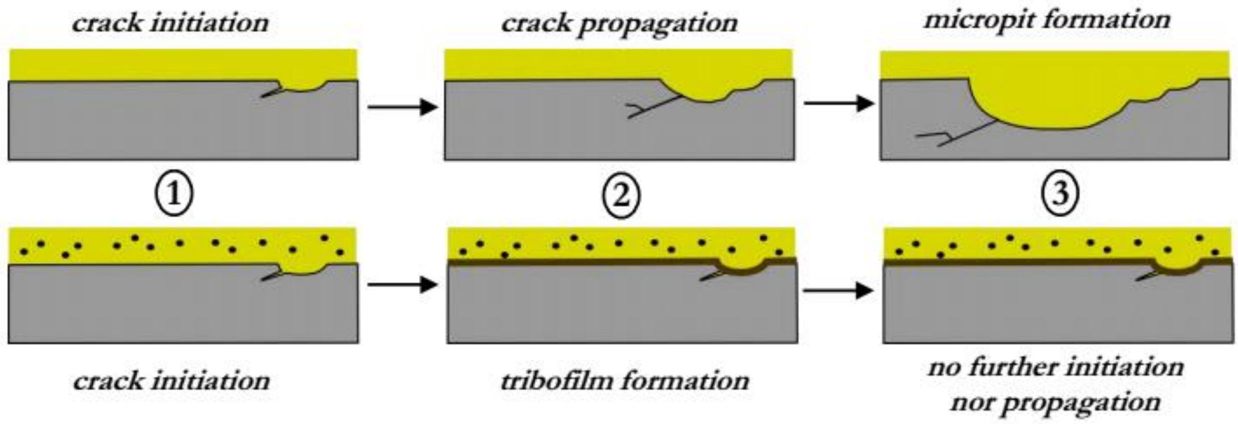


Fig. 14. Illustration of lubrication by base oil alone (top) and tribo-film formation and surface protection by nanoparticles (bottom) (Rabaso 2014).

8.3. Mending effect

The mending effect or self-repairing effect is characterized by nanoparticles deposition on the interacting surfaces and compensate for the loss of mass. During this phenomenon, the nanoparticles deposit on wear surface to reduce abrasion (Song et al. 2012). Nanoparticles in the lubricating oil have the ability to fill scars and grooves of the friction surface. **Fig. 15** shows the schematics of the friction surface where scars and grooves have been filled up with nanoparticles. Majority of studies reporting the mending effect, have used EDX analysis to confirm the deposition of nanoparticles on the rubbing surface.

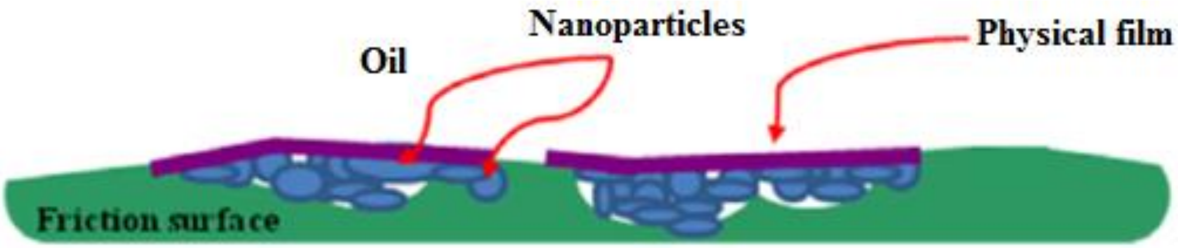


Fig. 15. Schematics of nanoparticles filled up in scars and grooves on friction surface (Choi et al. 2009).

8.4. Polishing effect

The polishing effect is believed to be reported when roughness of the lubricating surface is reduced by nanoparticle-assisted abrasion. Polishing effect is also termed as smoothing effect in various studies. In the tribological contacts, the nanoparticles may be filling-up the gaps of the rough asperities which may act as reservoirs of solid lubricants (nanoparticles) within the contact, as shown schematically in **Fig. 16** (Kalin et al. 2012). This process of filling up rough valleys is referred as the smoothing out process. This "artificial smoothing" or polishing mechanism lead to improved tribological performance mainly due to the reduced surface roughness (Kheireddin 2013). To characterize this effect, the surface topography analysis tools like AFM are found to be helpful as they can provide the effect of nanoparticles on surface roughness.

Fig. 16. Illustration of smoothing/polishing effect by filling up of rough valleys of rubbing surfaces (Kalin et al. 2012).

8.5. Investigation of lubrication mechanism

To investigate the lubrication mechanisms for lubricating oils enriched with nanoparticles, a number of surfaces characterization techniques have been used by researchers. The analysis techniques include scanning electron microscopy/energy dispersive spectrometer (SEM/EDS), atomic force microscopy (AFM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and Raman Spectroscopy (Alves et al. 2013; Chou et al. 2010; Demas et al. 2012; Ettefaghi et al. 2013; Ginzburg et al. 2002; Greenberg et al. 2004; Gulzar et al. 2015b; Hernández Battez et al. 2008b; Hu et al. 2011; Hu et al. 2002; Kolodziejczyk et al. 2007; Lee et al. 2009a; Lee et al. 2009b; Liu et al. 2005; Liu et al. 2004; Padgurskas et al. 2013; Peng et al. 2010b; Song et al. 2012; Thakur et al. 2016; Viesca et al. 2011b; Wu et al. 2007; Xiaodong et al. 2007). **Table 7** shows the summary of various studies mentioning the tested surfaces analysis technique and reported lubrication mechanism. However, it has been observed that due to existence of various lubrication mechanisms by nanolubricants, these surface analysis tools are not enough to distinguish the role of nanoparticles amongst these mechanisms. There are various studies which have reported multiple mechanisms for nanolubricants, an example has been given in **Fig. 12.** This situation become more complex when it has to draw a line between direct effect (e.g., ball bearing/tribo-film) of nanoparticles and the effects surface enhancement (e.g., mending/polishing) (Lee et al. 2009c).

Table 6 Summary of reported effects of nanoparticles on tribological properties, potential lubrication mechanisms and rubbing surfaces characterization.

Nanoparticle	Lubricant	Nanoparticle Role	Effect on Friction	Effect on Wear	Effect on EP	Mechanism	Surface Analysis Technique	References
Cu	PAO6	Antiwear, EP	-	Positive	Positive	Tribosinterization	SEM, EDS	(Viesca et al. 2011b)
Ni	PAO6	Friction Modifier, Antiwear, EP	-	Positive	Positive	Tribosinterization	SEM, EDS	(Chou et al. 2010)
ZnO, ZrO_2, CuO	PAO6	Antiwear, EP	-	Positive	Positive	Deposition	SEM, EDS	(Hernández Battez et al. 2008b)
Graphite	Supergear EP220	Friction Modifier, Antiwear	Positive	Positive	-	Polishing	SEM, AFM	(Lee et al. 2009a)
Fullerene, Carbon nanoballs	SAE-20W50	Antiwear	-	Positive	-	Mending	SEM	(Ettefaghi et al. 2013)
Al/Sn	SE15W/40	Antiwear, EP	-	Positive	Positive	Mending	SEM, EDS	(Liu et al. 2005)
Pb	TBA, liquid Paraffin	Friction Modifier, Antiwear	Positive	Positive	-	Ball bearing Tribo-film	SEM, EDS	(Kolodziejczyk et al. 2007)
Fe, Cu, Co	SAE10	Friction Modifier, Antiwear	Positive	Positive	-	Tribo-film	SEM, EDS	(Padgurskas et al. 2013)
Al	liquid Paraffin	Friction Modifier, Antiwear	Positive	Positive	-	Tribo-film	SEM, EDS	(Peng et al. 2010b)
CuO	SAE30	Friction Modifier, Antiwear	Positive	Positive	-	Ball Bearing, Mending	SEM, EDS	(Wu et al. 2007)
CuO, MoS_2	Palm TMP ester	Antiwear, EP	-	Positive	Positive	Mending, Tribo-film	SEM, EDS, Raman spectroscopy	(Gulzar et al. 2015b)
BN, MoS_2	PAO10	Friction Modifier, Antiwear	Positive	Positive	-	Tribo-film	Raman spectroscopy	(Demas et al. 2012)
MoS_2	SAE 20W-40	Friction Modifier, Antiwear, EP	Positive	Positive	Positive	Mending	SEM, EDS	(Thakur et al. 2016)
MoS_2	PAO	Friction Modifier, Antiwear, EP	Positive	Positive	Positive	Tribo-film	SEM, EDS	(Nallasamy et al. 2014)
MoS_2, TiO_2, MoS_2/TiO_2	liquid paraffin	Friction Modifier, Antiwear	Positive	Positive	-	Mending, Tribo-film	XPS	(Hu et al. 2011)
MoS_2	liquid paraffin	Friction Modifier, Antiwear, EP	Positive	Positive	Positive	Tribo-film	SEM, EDS	(Verma et al. 2008)
ZnO	60SN base oil	Friction Modifier, Antiwear	Positive	Positive	-	Mending	SEM	(Ran et al. 2016)
hBN	SAE 15W40	Friction Modifier, Antiwear	Positive	Positive	-	Ball bearing, Polishing	SEM	(Abdullah et al. 2014)
Magnesium borate	500 SN base oil	Friction Modifier, Antiwear, EP	Positive	Positive	Positive	Deposition, Tribo-film	SEM, XPS	(Hu et al. 2002)
Al_2O_3	SAE 15W40	Friction Modifier, Antiwear	Negative	Negative	-	Ploughing effect	SEM	(Abdullah et al. 2014)
CuO	liquid paraffin	Friction Modifier, Antiwear	Positive	Positive	-	Ball bearing	-	(Asrul et al. 2013)
WS_2	Jatropha TMP ester	Antiwear, EP	-	Positive	Positive	Tribosinterization	SEM	(Gulzar et al. 2015a)
ZnO, CuO	Mineral Oil	Friction Modifier, Antiwear	Positive	Positive	-	Deposition, Tribo-film	SEM, EDS	(Alves et al. 2013)
ZnO, CuO	PAO	Friction Modifier, Antiwear	Positive	Positive	-	Deposition, Tribo-film	SEM, EDS	(Alves et al. 2013)
ZnO, CuO	Sunflower Oil	Friction Modifier, Antiwear	Positive	Negative	-	Tribo-film	SEM, EDS	(Alves et al. 2013)
ZnO, CuO	Soybean Oil	Friction Modifier, Antiwear	Positive	Negative	-	Tribo-film	SEM, EDS	(Alves et al. 2013)
TiO_2	10W-30	Friction Modifier, Antiwear	Positive	Positive	-	Ball bearing, Deposition	-	(Laad and Jatti 2016)
CuO	Mineral Oil	Friction Modifier, Antiwear	Positive	Positive	-	Deposition, Polishing	SEM, EDS	(Jatti and Singh 2015)
$ZnAl_2O_4$	Lubricating Oil	Friction Modifier, Antiwear	Positive	Positive	-	Self-repairing effect, Mending	SEM, EDS	(Song et al. 2012)

9. Discussion

This paper has reviewed the main classes of nanoparticles as lubricating oil additive, focusing on published research that investigates tribological performance of these additives. It must be stressed that it covers the tribological role of nanoparticles only while linear nanostructures like nanotubes, nanorods, nanowires, nanosheets are not in the scope of this work.

The role of various factors like dispersion stability, nanoparticle concentration, morphology and experimental test conditions have been discussed. The interdependence of these factors make the nanoparticle a difficult choice than the conventional antiwear additives and friction modifiers.

While looking into dispersion stability behaviors of nanolubricants, the use of ultrasonic means of nanoparticles dispersion proved to be more effective than mechanical agitation methods. The research in surface modifications of nanoparticles paved a way towards stable suspensions. Oleic acid found to be effective surface modifying agent for different nanoparticles/base oils combinations. But the question of compatibility twofold when a researcher or tribologist has to look for appropriate surface modification for specific nanoparticle/lubricant combination i.e. after compatibility of nanoparticle/lubricant, which surfactant/surface modifying agent and modification method is to be chosen. But this multiple decision making is part and parcel for getting the stable nanolubricant which is a prerequisite for nanolubricant formulation due to many stationary applications.

For the suitable nanoparticle concentration, the question is two-pronged as optimum concentration is linked with dispersion as well as tribological performance. The process of getting suitable nanoparticle concentration was random as the chosen range of concentration was based on hit and trial methods in most of the cases while few have selected on the basis of previous studies. A low concentration range has been observed for chalcogenides, IF and carbon based nanoparticles as compared to metal oxide nanoparticles but it is not a fixed rule as nanolubrication is proved to be system specific. Generally, for all type of nanoparticles a concentration of less than 2 wt% has shown effective tribological characteristics.

For nanoparticles shape and morphology, the selection is proved to be more related to contact pressures they have to be undergone. Spherical and quasi spherical nanoparticles are found suitable to provide ball bearing effect between sliding surfaces provided the contact pressure should not damage their shape and structure. The linkage of nanoparticle size with dispersion by Stokes' law make it simple to link the size with dispersion stability of nanolubricant. By the simple equation, the smallest the size, better will be the dispersion stability and consequently improved tribological behavior. The layered structure of chalcogenides found to be more suitable for friction reduction by tribo-film formation. The comparatively recent class of inorganic IF nanoparticles has shown the lubrication advantages of ball bearing as well as protective film formation. They also proved to engage additional lubrication mechanisms of exfoliation. Once exfoliation occurs, IFs are believed to provide low shear-strength protective layer that adhere to the rubbing surfaces to reduce sliding friction. Other nanoparticulate solids also having layer-lattice structure like chalcogenides and boron nitride also tend to provide low friction most likely by similar mechanism (Spikes 2015).

While summarizing different experimental studies, many types of nanoparticle have been outlined as potential lubricant additives. Of these, metal oxides, chalcogenides, IF and carbon based nanoparticles have been used most widely. Metal nanoparticles and metal oxide nanoparticles have been found more suited as antiwear/EP additive than friction modifier due to high shear strength of tribo-films on the rubbing surfaces. In terms of friction reduction, chalcogenides, carbon based nanoparticles and IFs have been found more promising. They show improved friction behavior in boundary lubrication conditions during tribo-testing.

Sliding contact has been widely used and many studies have mentioned extreme pressure characteristics using four-ball tribo-testing.

A number of lubrication mechanisms have been reported in literature. In maximum studies combination of lubrication mechanisms have been reported in terms of primary direct effect (ball bearing/ tribo-film) and secondary surface enhancement (mending/polishing). Although a number of up to date surface analysis techniques have been used in variety of articles, but the explanation lubrication mechanism of nanoparticles based lubrication remained unclear and even mystifying in few cases. The complexity of lubrication mechanism increases for fully formulated lubricants as no such study has discussed the chemical interaction between existing additives and nanoparticles.

Apart from inherent complexity of nanolubricant formulation, the nanoparticles enriched lubricants have been tested and found appreciable in severe conditions like commercial diesel engines. Their lubrication performance proved them to be effective counterparts to conventional lubricants in various studies. The challenge is to transfer this behavior reliably to commercially viable lubricants while providing better tribological performance than conventional additives.

10. Conclusions

The tribological behavior and lubrication mechanisms of main classes of nanoparticles as lubricating oil additive have been reviewed. Though hundreds of reported studies have claimed improved tribological performance of nanoparticles enriched lubricating oils, the mechanism of nanoparticle lubrication is not completely understood. The lubrication mechanism of nanoparticles is found to be complex since there are hundreds of nanoparticles and each of them may work in different ways in diverse applications. Additionally, there are a number of challenges hardwired to their applications which must be addressed. The most important challenge and a prerequisite is to maintain dispersion stability of such nanolubricants for long duration. Various combinations of surfactants/nanoparticles as well as surface modification methods should be investigated for the stabilization of nanoparticles in variety of lubricating base oils.

Another associated challenge is the increased viscosity of lubricating oils by adding higher concentrations of nanoparticles. Such undesired variation in oil viscosity may result in a high pressure drop in the lubrication system, which can lead to higher energy consumptions. Thus, physicochemical properties must be in desired range while formulating a suitable nano-oil.

While going through the diverse research on nanolubricants, another grey area is the compatibility of such nanoparticles with lubricant’s additive package like detergents, dispersants, antioxidants, VI and corrosion inhibitors. According to authors, the related research will be more justified by using fully formulated lubricants with no antiwear/EP additives or friction modifiers to investigate the realistic tribological behavior of nanoparticles.

Acknowledgements

The authors would like to thank the University of Malaya, which made this study possible through the high impact research, Project title: "Development of Alternative and Renewable Energy Carrier" UM.C/HIR/MOHE/ENG/60.

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