Investigation of tribo-performance and rheological behavior of lubricants: influence of MoS_2 nano-particles

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Abstract

Flow behavior of lubricants is largely determined by rheological properties that in turn influence their tribo-performance behavior. Rheological parameters can be influenced by dispersing MoS_2 nano-particles in them. In order to study the effect of MoS_2 nano-particles on tribological and rheological properties of lubricants, two commercially available blended lubricants were selected as base oils with synthetic engine oils of SAE grades 5W40. They were blended with 0.15 and 0.2% by weight of functionalized nano-MoS_2. Standard ASTM and IS procedures were used to determine physicochemical properties and tribo-performance behavior of oils respectively. Rheometer Physica MCR 301 from Anton-Paar Austria was used to determine the rheological parameters of lubricants. A marginal reduction in friction to the tune of 3% has been observed for the 0.2 wt% of MoS_2 nano-particles in the tested lubricants while anti-wear properties showed significant enhancement by 20% indicating better anti wear properties of nano-MoS_2. Extreme pressure properties of MoS_2 particles play an important role in defining its anti-wear properties as it has significant load bearing properties. Rheological data reveal that tested MoS_2 nano-fluids show shear thinning behavior at all tested temperatures and rheological behavior improved with the addition of MoS_2 nanoparticles due to increase in apparent yield stress. Copyright © 2018 VBRI Press.

Keywords: Tribology, MoS_2 nano-fluids, four-ball tribo-tester, rheometer, engine oils.

Introduction

Nano-particles have gained popularity as additives in lubricant industry in the recent past as they influence the performance behavior of the lubricants **[1]** Choi blended nano-particles with the liquids and coined the term nano-fluids [2]. Nanoparticles influence heat transfer capabilities, tribological behavior and rheological behavior that in turn influence performance behavior of the lubricants and ultimately influencing the life of the machine.

A lot of research work has been carried out to study the influence of nanoparticles in the heat transfer properties of lubricants which largely depends on their thermal conductivity. Comprehensive reviews **[3-5]** throw sufficient light on this aspect in which details of theoretical models and experimental observations have been reported. Recently thermal conductivity of Co_3O_4 ethylene glycol-based nano-fluids has been studied and it was reported to be enhanced by 27% **[6]**. Heat transfer properties besides depending on thermal conductivity of nano-fluids, also depend on the flow behavior which is determined by rheological studies as the rapidity of the fluid motion helps dispose off the heat from the production site thus saving the machine component **[7]**.

Rheology is the study of flow and deformation behavior of matter. Rheology of lubricants generally excludes the study of low molecular weight liquids as they can be explained by Newtonian model **[8]**. Shear viscosity, thixotropy and linear Viscoelasticity of TiO_2 dispersed PEG200 suspension studies reported that presence of TiO_2 makes the flow non Newtonian with shear thinning behavior **[9]**. Viscosity of heat transfer oil with CuO, Al_2O_3 and TiO_2 nanoparticles studied by rheometer reported that the base fluid showed shear thickening (dilatant) behaviour while nano-fluids showed shear thinning (pseudo-plastic) behavior **[10]**. Rheology plays an important role to influence tribo-performance behavior of the lubricants.

Tribo-performance behavior of lubricants largely depends on the additive package which influences the film forming capabilities of lubricants and hence affects its anti-friction and anti-wear behavior. Nano-particles as additives have gained popularity as they influence the tribo-performance behavior of lubricants by varying degrees. Nano copper in this regard has been studied widely and found to have good anti-friction properties at higher loads and higher sliding speeds **[11]**. Nano Cu was also found to have better anti-wear and anti-friction properties than ZDDP **[12]**. Surface-modified Cu nanoparticles by dioctylamine dithiocarbamate (DTC8), tetradecyl hydroxamic acid and oleic acid have also been reported to possess good anti-wear and anti-friction properties on blending with lubricants **[13-15]**. 2-ethyl hexoic acid (EHA) surface-modified TiO2 nanoparticles blended with liquid paraffin was reported to have excellent load-carrying capacity, good anti-wear and anti-friction properties **[16]**. CuO, TiO_2 and nano-diamond as oil additives with base oil and API-SF engine oil were studied and were found to have significant anti-friction and anti-wear properties **[17]**. Size effects studies of SiO_2 nanoparticles as oil additives on tribology of lubricant reported that the optimal concentration of SiO_2 nanoparticles in liquid paraffin is associated with better tribological properties than pure paraffin oil **[18**]. MoS_2 micro-molecules have shown excellent anti-wear and anti-friction properties as an oil additive **[19]**. Rheological and tribological properties of lubricating oils containing platelet MoS_2 nanoparticles of average size 50 nm were studied and enhancement in tribo-performance behavior (anti-friction and anti-wear) was observed **[20]**.

Out of many nano-particles studied as oil additives, MoS_2 has shown promising results in enhancing the tribological performance besides Cu. However studies on MoS_2 nanoparticles as oil additives are scant and there is a scope to find an optimal dose of nano MoS_2 for much improved rheological and tribo-performance behavior. Hence present study is carried out to test MoS_2 nano-particle as an oil additive for the influence on rheological and tribological performance in the synthetic engine oils.

Experimental

Lubricant selection

Two synthetic commercial engine oils (diesel/gasoline) coded as CE and SH of SAE grade 5W-40 have been considered for the present study.

Preparation of surface modified MoS_2 nano-fluids

The surface modification technique involving two step method was employed to synthesize oleic acid coated MoS_2 nano-particles. The MoS_2 nano-particles were synthesized using hydrothermal method by chemical treatment of ammonium heptamolybdate, citric acid and sodium sulphide. Thus synthesized MoS_2 nano-particles were surface modified by using oleic acid. The surface modified MoS_2 nano-particles were blended with engine oil in different weight percentages. In order to facilitate proper dispersion of $MoS_{2,}$ blends were sonicated by using ultrasonic bath. The prepared MoS_2 nano-fluids were then kept under observation for examination of dispersion stability over a time period of 30 days. The physical observation reveals that there is no settling of MoS_2 nano-particles in the prepared MoS_2 nano-fluids. Therefore this technique produces the homogeneous and stable MoS_2 nano-fluids.

Lubricant characterization

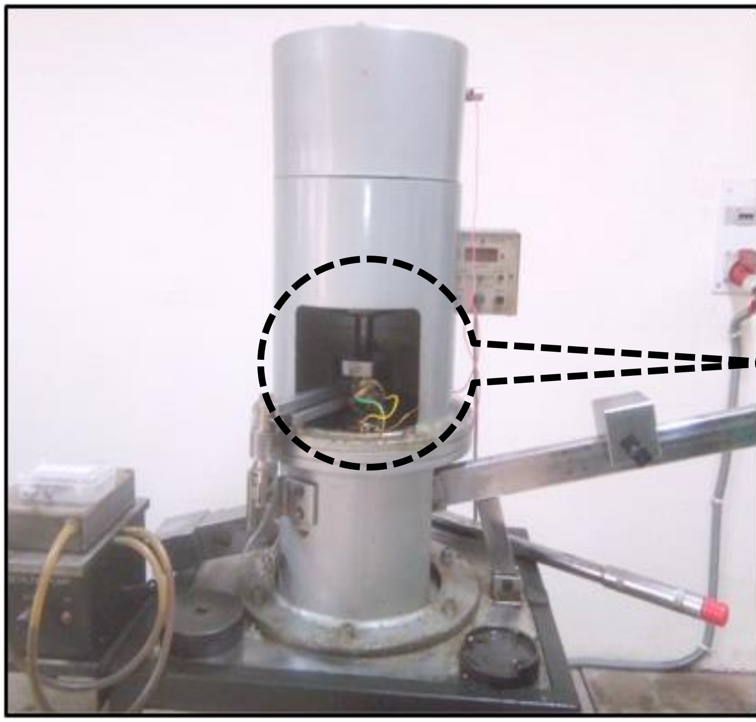
The selected lubricants have been characterized for their physico-chemical properties, tribological performance and rheological behavior. The physico-chemical properties provide the basic qualitative information on the lubricant blends, the tribological behavior provides the information on performance of lubricants while rheological properties provide information on the flow behavior of the lubricants.

Physico-chemical properties

Standard test procedures proposed in ASTM and Indian Standards (BIS) were used to measure physicochemical properties such as density, viscosity, viscosity index, sulphated ash, total acid number (TAN) and total base number (TBN) for determining qualitative information about the lubricants. TAN gives an idea of the acidic impurities present in the lubricant that may lead to corrosion of the components while TBN shows the capability of the lubricants to neutralize acids produced in the course of normal use of oil. Anti-wear additives and detergents present in the oil enhance performance of the oil and carry metallic elements that are measured by sulphated ash as well as by trace metal analysis. Trace metal analysis was carried out using Inductively coupled Plasma Atomic Emission Spectrometer (ICP-AES); model: PS 3000 UV (DRE), Leeman Labs Inc. (USA) was used to measure the presence of trace metals Zn, Mo and P in the oil. These metals are used for heat transfer purposes and as EP additives.

Tribo-performance investigation

Four Ball Tribo-tester (FBT) **(Fig. 1)** was used to determine tribo-performance behavior of the tested nano lubricants by using the standard wear test procedure as mentioned in ASTM D: 4172B. This will help understand the correlation between tribological properties and rheological properties of nano-fluids due to their direct mutual influence on each other. The FBT evaluates the anti-friction and anti-wear properties of lubricants. Four ball sliding contact geometry formed in between four balls each of diameter 12.7 mm is used in FBT. The four balls are assembled in a tetrahedron with bottom three balls fixed in the ball pot while the fourth ball is mounted on the vertical shaft and is free to rotate at a predefined spindle speed. The lubricant to be tested is introduced in the stationary ball pot forming thin lubricating film between the bottom three and the top ball. The contact friction in terms of frictional torque is continuously recorded during the entire test duration. The wear scar diameter (WSD) that determines the contact wear is measured at the end of the test using an industrial apochromatic stereo zoom microscope. Each of the oil is tested twice and the wear scar diameter along the vertical and horizontal axis is measured for all the bottom three balls thus providing 12 readings for given oil. The average of the 12 readings is reported as the WSD. The experiments are performed on balls made up of AISI chrome alloy standard steel No.E-52100, grade 25 EP (extra polish). Test conditions of tribological test ASTM D: 4172B include 40 kgf load, 75˚C temperature, 1200 rpm speed, test duration 1 hour.



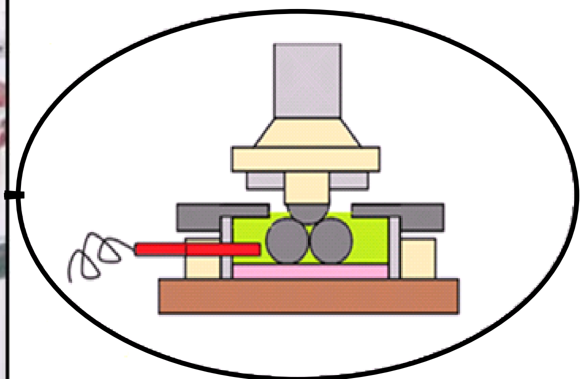


Fig. 1. Four ball Tribotester (FBT).

Fig. 2. Concentric cylindrical geometry of Rheometer.

Rheological properties of nano-fluids

The variation of Rheological parameters (viscosity, shear stress, compliance) with shear rate has been investigated using RHEOPLUS/32 MCR 301 from Anton Paar Austria. The Rheometer capable of performing rheological studies in rotational or oscillatory mode consists of an EC motor with a torque range of 10-200 mNm. The experiments have been performed using concentric cylinder geometry DG 26.7 as shown in **Fig. 2.** The space between the concentric cylinders was filled with the lubricant to be tested and the inner cylinder was rotated with the help of a spindle at the desired speed. Different sets of experiments were performed to determine the variation of coefficient of viscosity, shear stress and compliance with shear rate. The variation of shear stress with shear rate was observed for temperature 30-50˚C with 400 data points.

Results and discussion

The results obtained for the physico-chemical properties, friction and wear tests and rheological tests for the nano-fluids and base fluids are discussed below.

The physico-chemical properties of the nano-fluids as obtained from the standard tests are given in **Table-1**. Blending of 0.2% MoS_2 nano-particles in base fluids do not change the characteristic properties of base fluids and hence the nano-fluids too can be used for the similar application as the base fluids are used for. Lower TAN and TBN values can be attributed to nano particles addition to the base fluids while the minor changes in the values of density may be observed due to the instrumental/measurement errors.

Table 1. Physico-chemical properties of nano-fluids.

Characteristic Property	Lubricant Code			
	CE	CE+0.2 % MoS_2	SH	SH+0.2 %MoS_2
Density at				
15˚C(gcm^{-3})	0.865	0.866	0.853	0.851
30˚C(gcm^{-3})	0.863	0.864	0.850	0.848
Kinematic viscosity (mm^2/s)				
@ 40˚C	83.68	83.86	78.82	79.11
@100˚C	13.28	13.35	13.05	13.15
Viscosity index (VI)	162	161.4	166	168.5
TAN (mg KOH/g)	2.13	2.05	2.00	1.98

Trace metal analysis of the base lubricants reveal that the synthetic oils (tested lubricants) show high concentrations of Zn and P while almost negligible Mo as the values of trace metals for CE are Zn 907.10 mg/l, Mo 1.00 mg/l, P 857.90 mg/l while corresponding values for SH are Zn 924.26 mg/l, Mo < 1.00 mg/l and P 877.90 mg/l. The presence of these elements has shown enhancement in tribological performance in terms of anti-friction, anti- wear and extreme- pressure behavior.

The anti-friction and anti-wear behavior of the lubricants in general depicts their tribo-performance. **Fig. 3** shows the variation in coefficient of friction for the lubricants over the entire experimental duration. It is observed that the coefficient of friction is higher at the early stage due to the static friction, which decreases in due course of time. However, the contact friction starts to increase at a later stage due to the initiation of the wear scar on the ball surfaces. Further, due to the smoothening of the worn out surfaces and due to the formation of boundary films the coefficient of friction became almost constant. The coefficient of friction at the end of the test for the base lubricants has been recorded to be 0.089 for lubricant CE and 0.088 for lubricant SH. Blending of MoS_2 nano-particles in varying concentrations has resulted in reduction in kinetic friction. In case of lubricants CE and SH the friction decreased monotonically though marginally for the 0.10% and 0.15% and 0.20% for MoS_2 nano-particle concentrations. The lowest values of friction coefficient observed are 0.086 and 0.085 for the lubricants CE and SH respectively. Lower influence of MoS_2 nano-particles on COF may be attributed to the presence of additive package in the base lubricant. Lower wt percentage of nano MoS_2 particles may also be the reason for the same.

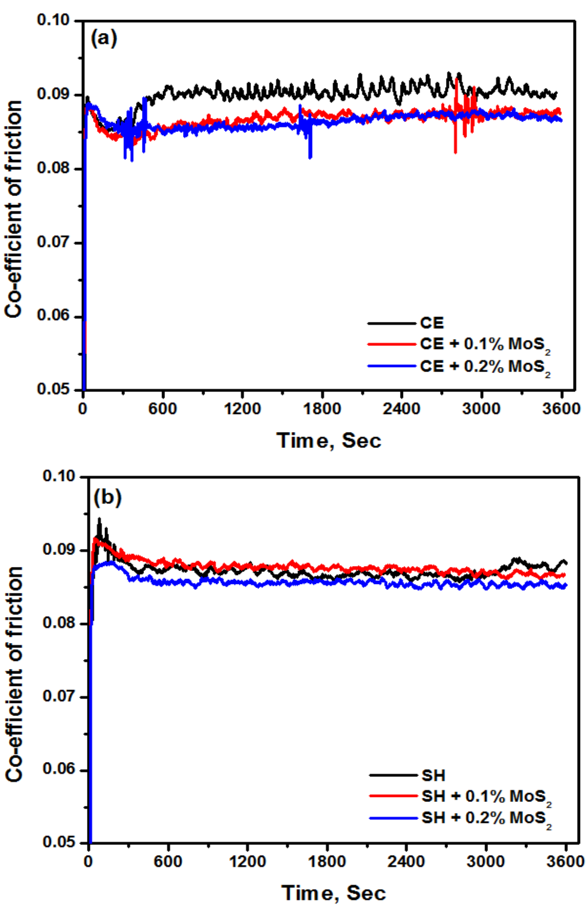


Fig. 3. Friction behavior for the lubricant blends of CE and SH oils.

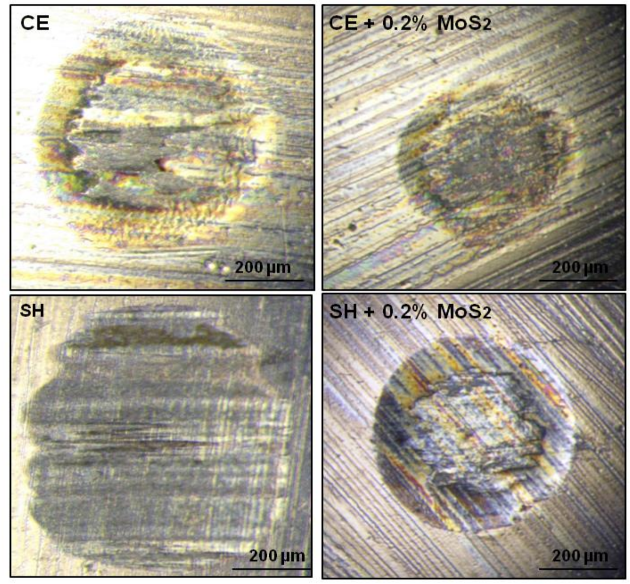


Fig. 4. Wear scar diameters for the Lubricants (a) CE, (b) CE+0.2% MoS_2, (c) SH, (d) SH+0.2% MOS_2

Table 2. Tribological & Rheological performance of lubricants.

Tribological performance					Rheological performance		
Lubricant	COF (μ)	WSD (mm)	% change in COF & WSD w.r.to base oil		Apparent yield stress in Pa at different Temperature (°C)		
			(μ)	WSD	30°C	40°C	50°C
CE	0.089	0.39	-	-	33.6	22.2	16.7
CE+ 0.1% MoS_2					34.4	22.7	17.4
CE+ 0.2% MoS_2	0.086	0.336	2.8	14.1	37.4	25.7	18.8
SH	0.088	0.446	-	-	33.3	20.8	14.4
SH+ 0.1% MoS_2					36.2	23.1	16.3
SH+ 0.2% MoS_2	0.085	0.357	3.2	20.0	39.3	25.6	18.0

The anti-wear behavior of the lubricants recorded in terms of the wear scar diameter (WSD) reveals **(Fig. 4)** that the lubricants CE and SH have a wear scar diameter of 0.391mm and 0.446 mm respectively. The blending of MoS_2 nano-particles in varying concentrations has resulted in reduction in wear scar diameter for both the lubricants. The wear scar diameter monotonically decreased with increase in the concentration of MoS_2 nano-particles. The lowest values of wear scar diameter observed are 0.336 mm and 0.357 mm for the lubricants CE and SH respectively at 0.20% concentration of MoS_2 nano-particles. For a better comparison of the tribo test results, the friction and wear scar diameter are tabulated in **Table 2**. The wear scars as observed on the ball test specimens are shown in figure 4. The morphology of wear scar reveals the normal rubbing wear in between the contact. With the increase in the percentage of the nano MoS_2, WSD shows a decrement indicating the improvement in the anti-wear properties of the lubricants as the nanoparticles help improve the film forming capability. **Fig. 5** shows the trend for variation in coefficient of friction and WSD with increasing percentage of MoS_2 nano-particles in the base oils. For the lubricant CE the highest friction reduction though marginal was reported for 0.20% of nano MoS_2 concentration with a 3% decrement while for 0.1% concentration it was negligible (1.5%). Similar trends were observed for SH with 0.1% and 0.2% nano MoS_2 concentrations with percentage decrease of about 1.6% and 3% respectively. In case of anti-wear behavior, the wear scar diameters keeps on reducing with increase in the concentration of the MoS_2 nano-particles. A reduction to the order to 11% and 14% observed in case of wear scar diameter with the addition of 0.1% and 0.2% MoS_2 nano-particles in lubricant CE while for the lubricant coded as SH same concentrations resulted into the decrement of WSD by 15% and 20% respectively.

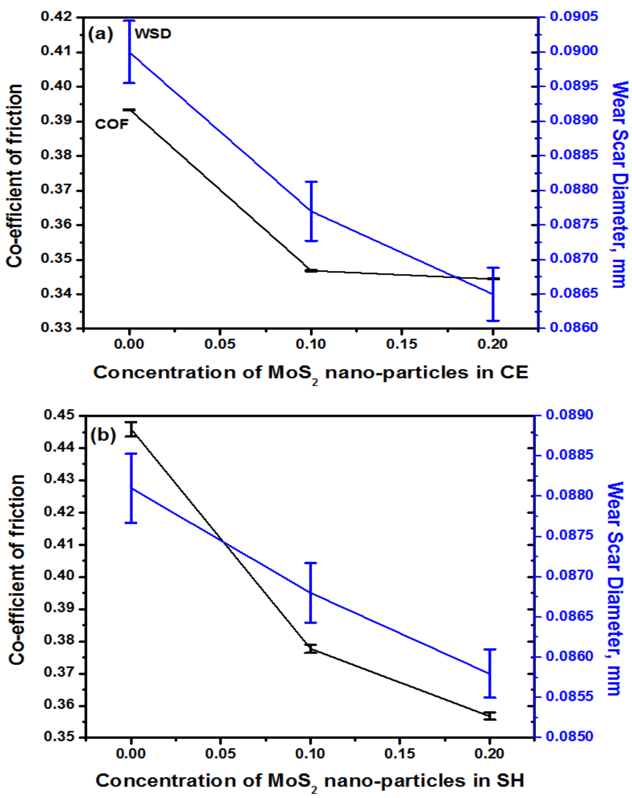


Fig. 5. Variation in friction and wear of CE & SH oils with changing concentration of MoS_2 nano-particles

Comparative assessment of anti-friction and anti-wear behavior is shown in **Table-2**. Blending of 0.1% and 0.2% MoS_2 nano-particles in the base fluids decrease the kinetic friction values to 0.088 and 0.086 respectively from 0.089 for lubricant CE and 0.087 and 0.085 respectively from 0.088 for lubricant SH.

Wear scar diameter (WSD) represents the anti-wear behavior of the lubricant samples. The ball specimens lubricated with CE show decrease in WSD to 0.346 mm and 0.336 mm from 0.391 mm for 0.1% and 0.2% of MoS_2 nano-particles concentrations respectively. Similarly for lubricant coded SH, WSD decreases to 0.378 mm and 0.357 mm respectively from 0.446 mm on blending the lubricants with 0.10% and 0.20% MoS_2 nano-particles. Blending of 0.10% and 0.20% MoS_2 nano-particles results in almost 11% and 14% reduction in wear in case of CE oil while a reduction to the order of 15% and 20% in wear is observed in case of SH oil respectively.

Blending of 0.10% and 0.20% MoS_2 nano-particles in base fluids enhances the anti-friction properties of lubricants marginally because of the presence of already existing additive package in the finished base oils and also due to addition of nano MoS_2 by small amount, yet it is sufficient enough to enhance the anti-wear properties up to 20%.

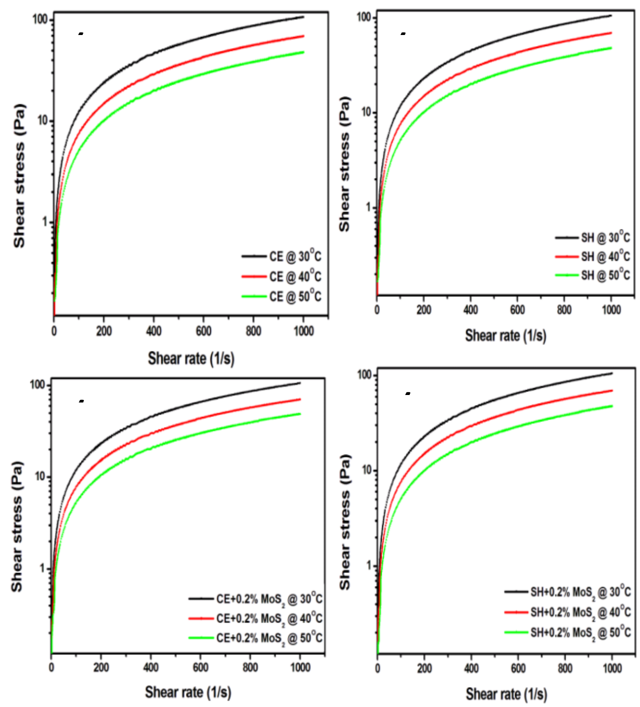


Fig. 6. Variation of Shear stress with shear rate for lubricant CE & SH (a) CE (b) SH (c) CE+0.2% MoS_2 (d) SH+0.2% MoS_2.

Flow curves shown in **Fig. 6** gives the rheological behavior of the lubricant specimens in terms of variation of shear stress with shear rate at 30, 40 and 50˚C temperatures for lubricants coded as CE and SH respectively. Shear stress is taken on the logarithmic scale while shear rate on the linear scale. Tested samples do not show initial yield stress, yet the rate of increment of shear stress with respect to shear rate decreases beyond apparent yield stress showing shear thinning behavior. Apparent yield stress is calculated by drawing a tangent on the linear portion of the curve in higher shear rate region and noting the shear stress where it touches the shear stress axis. Variation in apparent yield stress with variation in concentration of MoS_2 nano-particles is shown in **Table-2**. Apparent yield stress increases with the increment in the concentration of the MoS_2 nanoparticles monotonously which is accorded with the increase in kinematic viscosity on blending the nanoparticles with the base fluid (Table-1). Apparent yield stress for CE is more than SH at all concentration and temperatures. **Fig. 6(a)** and **6(b)** represent the shear stress vs shear rate variation of CE and SH base lubricant samples @ 30, 40 and 50˚C respectively. Lower value of apparent yield stress at higher temperatures is a sign of decrease in viscosity. More over rate of decrement of shear stress with respect to shear rate is also pronounced indicating increment in rate of shear thinning behavior. **Fig. 6(c)** and 6(d) represent the shear stress vs shear rate graphs @ 30, 40 and 50˚C for CE+ 0.2% MoS_2 and SH+0.2% MoS_2 respectively. It is obvious from the graphs and corresponding apparent yield stress values in **Table-2** that the rate of enhancement of apparent yield stress increases with the increase in concentration showing better binding of nano-particles with the base fluid molecules. It is also obvious that rate of decrement of apparent yield stress with temperature decreases on increasing the concentration of nanoparticles. It shows that nanoparticles not only increase the viscosity of lubricants, they also play important role in arresting the decrement rate of viscosity at higher temperatures.

Conclusion

In the present research work the lubrication capabilities of Cu nano-fluids have been experimentally investigated. The functionalized MoS_2 nano-particles were efficiently dispersed in commercial synthetic lubricants in 0.10% and 0.20% concentrations respectively and its influence on the friction, wear and rheological behavior has been studied. On the basis of the investigations following salient conclusions are made;

- Blending of MoS_2 nano-particles in 0.20% concentrations do not alter the physicochemical properties of base fluids.
- The MoS_2 nano-fluids result in marginally enhancing the anti-friction behavior, however anti-wear behavior of lubricants reported up to 20% enhancement. The addition of MoS_2 nano-particles aid in formation of boundary films on the functional surfaces thereby resulting into reduced wear. The extent of damage severity too decreases with the blending of MoS_2 nano-particles in the base fluid.
- Out of the two lubricants selected the blends of MoS_2 nano-particles in SH have reported the best tribological performance due to the inherent physico-chemical properties and additive concentration of the base fluid.
- Apparent yield stress increases monotonically with increase in the concentration of MoS2 nano-particles in the base lubricants up to 0.2% showing increase in viscosity.
- Rate of shear thinning increases with temperature but decreases with increasing the nano particle concentration at same temperature.
- Base lubricants and nano-fluids show shear thinning behavior.
- Nanofluids increase the viscosity and decrease the rate of decrement of viscosity hence improving rheological behavior

Author’s contributions

Coceived the plan: PT, GDT, AKJ; Performed the experiments: PT, AK, Data analysis: PT, AK, GDT; Wrote the paper: PT, GDT. Authors have no competing financial interests.

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