Behavior of Composite Nanofluids Under Extreme Pressure Condition

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Abstract

Nanofluids of copper nanoparticles and Multi-walled carbon nanotubes (MWCNTs) have been studied separately in the past. They show excellent tribological properties. The main objectives of the present work are to synthesis and evaluate the tribological properties of nanofluids which is made of base oil, Cu nanoparticles and MWCNTs. Nanofluids with different concentrations were prepared using UP400S ultrasonicator from Hielscher. The extreme pressure (EP) and anti-wear (AW) properties were studied using Four Ball Tester TR30 L from Ducom according to ASTM D 2783 and ASTM D 4172 B respectively. All the concentrations improved the EP behavior. However, AW performance decreases indicating that these nanofluids are not suitable for low pressure (392 N) applications.

Keywords: Cu nanoparticles; EP and AW properties; four ball tester; Lubrication; MWCNTs; ultrasonicator

1. Introduction

The limitations posed by organic additives such as sulphur, phosphorus or chlorine containing compounds have great challenges to meet stringent requirements of modern machinery. These additives react with metal surfaces chemically and consume some metal by forming easily sheared layers of sulphides, phosphides or chlorides. Moreover, these elements being 'active' have adverse effects on environment. Therefore, substitution of these additives is very much necessary.

With the advancement of Nanotechnology, researchers have found that inorganic nanomaterials can be promising substitute and it has been a hot research topic for the last few decades [1]. Inorganic nanomaterials such as MoS_2 nanotubes [2], Ni [3], diamond and SiO_2 [4], fullerene [5], carbon onion [6], CuO [1], graphite nanosheets [7], WS_2 [8], magnesium borate [9], lanthanum borate [10], copper [11-17] and MWCNTs [18-20] have excellent tribological properties when used as an additives. However, no literature is available yet wherein two nanomaterials are added to base oil. Therefore, it is very important to study the tribological effects when two nanomaterials are added to base oil.

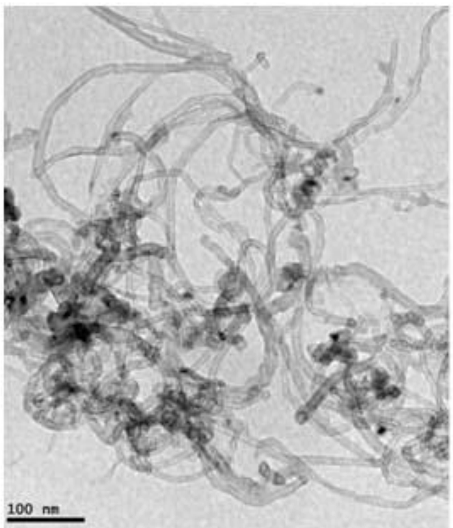
Nanofluids (*NANO*particles *FLUID S*uspension) are engineered colloids made of a base fluid and nanomaterials. The base fluid can be any fluid such as water, oil, organic solvent etc. and on the other hand nanomaterials can be any material whose at least one dimension is in 1 to 100 nanometer (10^{-9} m). Thus in terms of nanotechnology, addition of these additives (Cu and MWCNTs) to oil rendered nanofluids. In the present work, the nanofluids so made is called composite nanofluids because two different type, Cu and MWCNTs, of nanomaterials have been added to the base oil.

2. Experimental

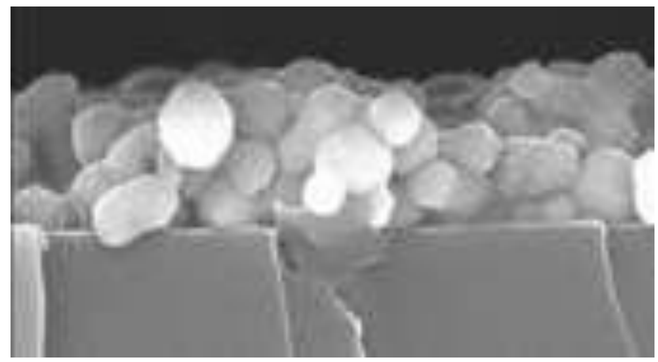
2.1 Nanaomaterials and base oil

A very weak concentration (0.1%) is sufficient to obtain interesting tribological properties even at extreme pressure condition [21]. Therefore MWCNTs was selected. To enhance the dispersion of MWCNTs in oil, it has been stabilized with anime group. It was purchased from Quantum Materials Co., Bangalore. The TEM image provided by supplier is shown in Fig. 1 (a).

Addition of copper nanoparticles into lubricating oils will lead to the formation of copper tribo-film at flash temperature preventing wear of tribo-pair [15]. Hence, copper nanoparticle was selected. It has been stabilized



(a)



(b)

Figure 1.TEM images of nanomaterials: (a) MWCNTs and (b) Cu

with oleic acid to prevent agglomeration. It was purchased from Reinste Nano Venture Ltd., New Delhi. The TEM image of Cu nanoparticles provided by supplier is shown in Fig. 1 (b).

Monograde oil with minimum amount of additives so as to prevent destabilization of nanofluids is chosen. Hence, commercially available monograde diesel oil (SEA40) is the right candidate for base oil. Shell Rimula R1 was selected as base oil. The main properties of the nanomaterials and base oil are given in the Table 1.

2.2 Synthesis of Nanofluids

The equipment used for the synthesis of nanofluids is UP400S ultrasonicator from Hielscher. The procedure followed for dispersion of nanomaterials is two step method as per “Protocol for Nanoparticle Dispersion” released by Nanotechnology Industry Association, UK [22]. The mass of nanomaterials for required concentration (wt %) is calculated based on mass of required volume of base oil. It is then transferred to steel glass and thoroughly mixed with 10 ml of base oil using spatula to break visible agglomeration. The remaining oil is added and stir well with a clean spatula. Steel glass is used to dissipate heat faster which is generated during sonification. The steel glass is introduced into ice-bath and fixed to a rigid stand. The sonicator probe is introduced into steel glass upto at least 1cm gap between probe face and bottom of steel glass. Sonication parameters are set as follow: amplitude 100% and operation mode 30% cycle. The sample is then sonicated for 30 minutes during which temperature was scan for every 5 minutes not to exceed 50˚ C. Thus nanofluids of different concentrations were prepared. Their concentrations and nomenclatures are given in Table 2. The stability of nanomaterials in base oil was evaluated. A small drop of nanofluids was dropped on glass slice and was let dry at room temperature and then characterized with metallographic microscope.

2.3 Extreme pressure test machine and procedure

All test components (4 balls, ball pot and collet) were cleaned thoroughly with hexane solution 2 to 3 times. The test rig used for extreme pressure tests (ASTM D2783) [23] was Four Ball Tester TR 30 L from Ducom Instruments Pvt. Ltd. The 12.7 mm test ball used in the study is made from AISI 52100 steel with a hardness of 65 HRc. The machine and test lubricant are brought to 18 to 35˚ C. The spindle speed is set to 1770 RPM. In this technique, one steel ball under load is rotated against three steel balls held stationary while immersed in the test lubricant. A series of 10 tests of 10-s duration are carried out at logarithmically increa-

Table 1. Properties of materials used.

Materials	Properties				
Nanomaterials	**Morphology**	**Purity (wt.%)**		**Size (nm)**	**Stabilizer**
Cu nanoparticles	Spherical	99.0		20-40 nm	oleic acid
MWCNTs	Tubular	95.0		8 nm inner dia., 12 nm outer dia., 4-5 micrometer length	Amine group
Base Oil	**SAE grade**	**Viscosity (cSt)**		**Viscosity Index**	**Density at 15˚C (Kg/l)**
		40˚C	**100˚C**		
Rimula R1, Shell	40	140	14.5	102	0.895
Test Balls	**Chemical compositions**				
AISI 52100	.98-1.1% C, 0.15-0.30% Si, 0.25-0.45% Mn, 1.30-1.60% Cr, <0.025% P, 0.025% S				

sing loads until welding occurred. The first run was made at an initial load of 490N and the additional runs were carried out at consecutively higher loads according to the standard method: 617, 980, 1235, 1568, 1960, 2450, 3087N. . . until welding occurs. If ten loads have not been run when welding occurs, the total was brought to ten by assuming, according to the standard, that loads below the last non-seizure load produce wear scars equal to the compensation scar diameter. The wear scar diameters (WSD) in the stationary balls were measured using optical microscope. From the EP results, the following parameters were obtained: last non-seizure load (LNSL), weld load (WL) and load-wear index (LWI). Repeatability and reproducibility were verified according to ASTM D 2783.

2.4 Hertz line

The Hertz line was obtained by plotting the Hertz scar diameter against the load. The Hertz scar diameter (D_h) is the average diameter of an indentation caused by the deformation of the balls under static conditions.

$$D_h = 8.73 \times 10^{-2} (P)^{1/3} \qquad (1)$$

where:
D_h = Hertz scar diameter, and
P = the static load applied.

2.5 Compensation line

The compensation line was obtained from a plot of the compensation scar diameters against the applied load. The compensation scar diameter is the average diameter of the wear scar on the stationary balls, caused by the rotating ball under an applied load in the presence of lubricant, but without causing either seizure or welding.

2.6 Last nonseisure load (LNSL), initial seizure load (ISL) and weld load (WL)

The last non-seizure load is the load at which the measured scar diameter is not more than 5 % above the compensation line. The initial seizure load is the load at which there is momentary break down of the lubricating film. The weld load is the lowest applied load in kilogram at which the rotating ball welds to the three stationary balls, indicating the extreme pressure level of the lubricant force has been exceeded. Usually, the region beyond the LNSL is known as *extreme pressure region*, whereas the region before the LNSL is the *anti-wear region*.

2.7 Load-wear index (LWI)

The *load-wear index (LWI)* is an index of the ability of lubricant to minimize wear at applied load. It is a single parameter that shows the overall EP behavior in a range between well below seizure and welding. Higher is the value of LWI, better is the EP property. It may be calculated from the expression:

$$\text{LWI (kgf)} = \frac{A}{10} \qquad (2)$$

Where:

A = sum of the corrected loads determined for the ten applied loads immediately preceding the weld load.

Corrected Load is the load in kilograms-force (or newtons) for each run obtained by multiplying the applied load by the ratio of the Hertz scar diameter to the measured scar diameter at that load. It is calculated for each applied load between the last non-seizure load and weld point using the equation:

$$\text{Corrected load} = \frac{LD_h}{X} \qquad (3)$$

where:
L = applied load
Dh = Hertz scar diameter, mm, and
X = average scar diameter, mm.

Table 2. Nomenclature of nanofluids samples as per Concentration.

Sl. No.	Concentration	Name
1	Base oil	BO
2	0.5 wt % MWCNTs	5M
3	0.5 wt % Cu	5C
4	0.5 wt % MWCNTs + 0.5wt % Cu	5M5C
5	1.0 wt % MWCNTs + 1.0 wt % Cu	10M10C

2.8 Anti-wear test machine and procedure

The test rig, tests balls and cleaning procedure is same as EP tests. As per ASTM D 4172 B [24], the fourth ball, referred to as the top ball, is pressed with a force of 392 N into the cavity formed by the three clamped balls for three-point contact. The temperature of the test lubricant is regulated at 75°C and then the top ball is rotated at 1200 rpm for 60 min. The wear scar diameters of the lower 3 balls were measured using optical microscope. This test also provides co-efficient of friction. Lubricants are compared by using the average size of the scar diameters worn on the three lower clamped balls.

3 Results and discussions

3.1 Micrographs of Nanomaterials in base oil

The images taken with the metallographic microscopy are shown in Fig. 2. The microscope cannot resolve the nanomaterials, however it enables the agglomeration state of the suspensions at micrometer scale. Cu nanoparticles shows less agglomeration than any other suspension as seen in Fig. 2 (a) and this can be accounted by its smaller size (20-40 nm). On the other hand, Fig. 2 (b) reveals the aggregate size of MWCNTs. Some agglomerations are seen with larger size than average aggregate size which may be due to micrometer length of MWCNTs resulting into agglomeration. Fig. 2 (c) and 2 (d) show large aggregates. This is due to attractive force between oleic acid and amine group which are used as stabilizer for Cu nanoparticles and MWCNTs respectively.

3.2 Extreme pressure properties

Table 3 represents the summary of extreme pressure properties of the nanofluids being tested. It clearly shows that all the nanofluids have shown higher weld load than base oil. The highest weld load is shown by 10M10C which confirms that higher concentration has better EP properties. 5M, 5C and 5M5C have same weld load which reveals that addition of two nanomaterials, composite nanofluids, has no effect on EP properties. The variation of LWI with concentration is shown in Graph 1. All the nanofluids improve the LWI, which means that all the nanofluids have the ability to reduce wear at applied load. Graph 2 shows the effect of concentration on LNSL and WSD. The WSD at LNSL of all the nanofluids is higher than that of base oil. This is due to increase in applied load. Though WSD of 10M10C is the highest but this is justified by its high weld load.

3.3 Anti-wear properties

Table 4 shows the summary of anti-wear properties of nanofluids being tested. The anti-wear properties of all the nanofluids are inferior to that of base oil as shown in Graph 3. The WSD of all the nanofluids are higher than that of base oil which means that excessive wear occur in the presence of nanomaterials. It may be due to low load applied during the test. At low load cooper nanoparticles may not peel off its oleic acid coating and again at low load heat generated is insufficient to melt

Table 3. Extreme pressure properties of tested nanofluids.

Lubricants	Initial Seizure Load, LNSL (N)	Mean Wear Scar Diameter (WSD) at LNSL (mm)	Weld Load (N)	Load-wear Index (N)
BO	1235.6	0.495	1569	480.54
5M	1569	0.566	1961.2	603.29
5C	1569	0.553	1961.2	600.06
5M5C	1569	0.556	1961.2	599.32
10M10C	1961.2	2.46	2451.5	810.75

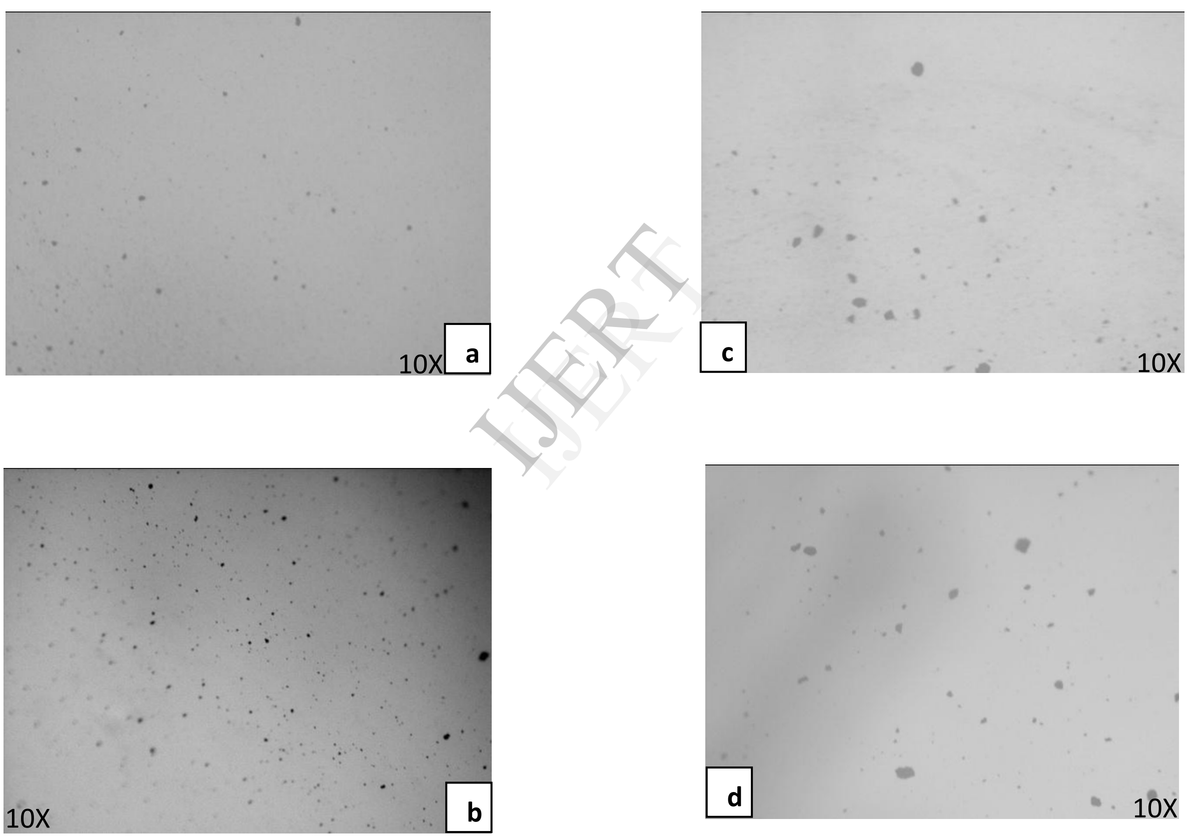
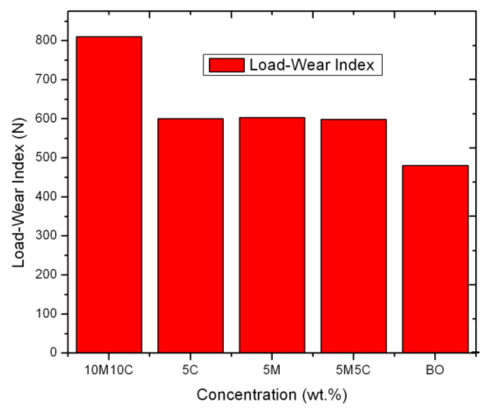
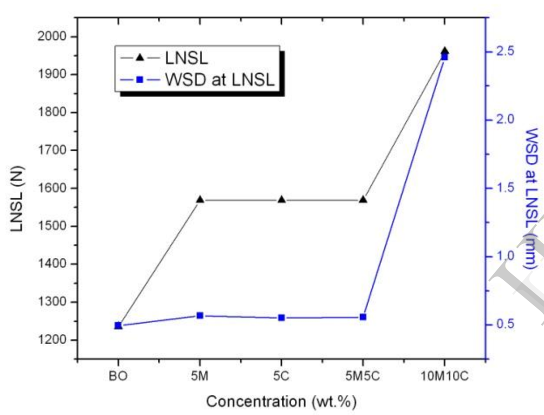


Figure 2. Metallographic micrographs of nanofluids: (a) 5C (b) 5M (c) 5M5C (d) 10M10C



Graph 1. Variation of LWI with concentration.



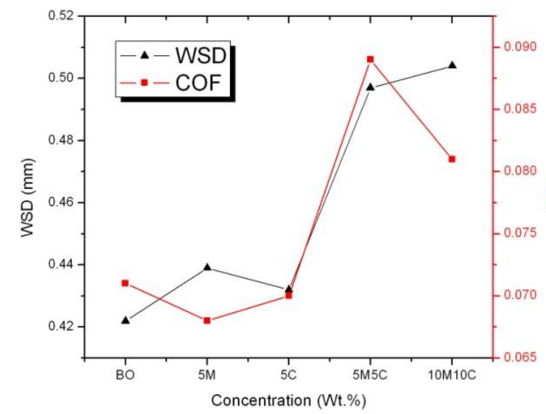
Graph 2. Effect of concentration on LNSL and WSD at LNSL.

Table 4. Anti-wear properties of tested nanofluids.

Nanofluids	WSD	COF*
BO	0.4219	0.071
5M	0.439	0.068
5C	0.432	0.07
5M5C	0.497	0.089
10M10C	0.504	0.081

* co-efficient of friction

the copper nanoparticles. It was anticipated that Cu nanoparticles will melt and coat the tribo-pair surface. However, it has to be yet verified at higher load. Since it fails to melt, therefore we can assume that the nanomaterials act as an abrasive. On the other hand, MWCNTs due to agglomeration also act as abrasive rather than acting as nano-bearing. This will results into



Graph 3. Effect of concentration on WSD and COF.

mixed type of wear i.e. adhesive wear and abrasive wear. Therefore, excessive wear occur and leading to increase in WSD. 10M10C shows the highest WSD due to higher concentration. The COF also shows no improvement accept 5M which is about only 4.2 % which cannot be considered as an improvement. The effect of concentration on WSD and COF is given in Graph 3.

4. Conclusions

The following conclusions are drawn from the results presented above:

- Nanofluids with different concentrations and different nanomaterials were synthesized using ultrasonicator.
- The micrographs of nanomaterials in base oil show some agglomeration in 5M and 5C, however, 5M5C and 10M10C shows larger agglomeration.
- The load carrying capacity of nanofluids were found to be improved.
- LWI, the ability of lubricant to minimized wear at applied load, of nanofluids were found to be improved with increasing concentration.

- Composite nanofluids i.e 5M5C has same EP properties with that of 5M and 5C which means that composite nanofluids does not improve EP properties.

- WSD of nanofluids at low load (392 N) were greater than that of base oil. Therefore, nanofluids are not suitable for low load applications.

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