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Research Article

Effect of Size of Multiwalled Carbon Nanotubes Dispersed in Gear Oils for Improvement of Tribological Properties

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The aim of the paper is to investigate the effect of size of multiwalled carbon nanotubes (MWCNTs) as additives for dispersion in gear oil to improve the tribological properties. Since long pristine MWCNTs tend to form clusters compromising dispersion stability, they are mildly processed in a ball mill to shorten the length and stabilized with a surfactant before dispersing in lubricant. Investigations are made to assess the effect of ball milling on the size and structure of MWCNTs using electron microscopy and Raman spectroscopy. The long and shortened MWCNTs are dispersed in EP 140 gear oil in 0.5% weight. The stability of the dispersed multiwalled carbon nanotubes is evaluated using light scattering techniques. The antiwear, antifriction, and extreme pressure properties of test oils are evaluated on a four-ball wear tester. It is found that ball milling of MWCNTs has a strong effect on the stability and tribological properties of the lubricant. From Raman spectroscopy, it is found that ball milling time of up to 10 hours did not produce any defects on the surface of MWCNTs. The stability of the lubricant and the antiwear, antifriction, and extreme pressure properties have improved significantly with dispersion shortened MWCNTs. Ball milling for longer periods produces defects on the surface of MWCNTs reducing their advantage as oil additives.

1. Introduction

Gear oils used in industries and automotive engines are often subjected to heavy loads, due to which they experience high temperatures and pressures causing higher friction and surface damage leading to failure of the system. To prevent failure, conventional engine and gear oils are dispersed with extreme pressure (EP) and antiwear (AW) additives that react chemically with the metal surfaces, forming easily sheared layers and thereby preventing severe wear and seizure. Allotropes of carbon such as graphite, fullerenes, carbon nanotubes, and graphene have attracted the interest of the researchers due to their special properties. The hybridization of the atomic orbital of carbons in carbon nanotubes and fullerenes is of type *sp*2, similar to that of graphite, making a perfect hexagonal array of atoms. The *sp*2 C–C bond of CNTs is considered one of the strongest in solid materials; thereby CNTs are expected to yield exceptionally good mechanical properties. Lubricants dispersed with allotropes of carbon are being extensively studied for their lower friction coefficients, thereby improving antiwear properties. MWCNTs possess large surface area compared to many inorganic nanomaterials and can be very easily surface-modified. Several novel studies are made on the effect of dispersion of multiwalled carbon nanotubes on the wear and friction characteristics of lubricants. The length of the nanotube synthesized by existing methods is known to be thousands of times larger than their width and thus limits their functionality for many applications. Owing to their large length to diameter ratios, MWCNTs despite use of surfactant tend to form agglomerates faster, thereby leading to them settling in the liquid medium. This aspect is a main challenge in obtaining stable dispersion in liquid medium. The most common and frugal method to reduce the size of MWCNTs is ball milling which shortens the length of MWCNTs and obtaining open ends. However, ball milling for extended period produces defects and damages the graphite structure rendering it useless for dispersion in lubricants. Studies are made on the effect of ball milling on the structure and defect generation. Pierard et. al. [1] studied the effect of ball milling on the structure of single-walled carbon nanotubes. Raman spectroscopy was employed to study the defects produced in various hours of ball milling time. It is found that there exists an optimum time to keep the tubular structure intact without defects. In case of single-walled carbon nanotubes, ball milling times of over 50 hours completely destroy the structure producing amorphous carbon. Dresselhaus et. al.[2], Cancado et. al. [3], and Paton et. al. [4] suggested methods to detect defects and evaluate purity of carbon nanotubes and graphene. It was proposed that the intensity of G-band and the D/G ratio can be highly useful to determine both the purity and the defect density of carbon nanotubes and graphene. Chen et. al. [5] first studied the effect of dispersed of ball-milled and stearic acid modified multiwalled carbon nanotubes (MWCNTs) on the stability and thereby improvement in the lubricating properties of liquid paraffin base oil. The friction and wear tests were conducted on a pin-on-plate wear-testing machine. It is found that ball-milled MWCNTs could form stable suspensions and improve the antiwear and antifriction properties. Engine oils dispersed with nanomaterials are investigated for tribological property enhancement by several researchers. A detailed review of the prior art is listed in Table 1.

As given in Table 1, most of the studies were done with dispersion of larger amounts of MWCNTS in base lubricants or paraffinic oils without additives. Only few studies were made on commercial grade formulated lubricating oils. Further in the studies, due to dispersion of MWCNTs in higher concentrations, the viscosity of the lubricant is found to be significantly enhanced. This enhancement in viscosity is the major reason for the improved tribological properties. Furthermore higher concentrations of any nanomaterials may lead to faster agglomeration rates and the stability of the suspension will get compromised. Since MWCNTs have long length ranging from 1 to 25 microns and diameter in nanometers, there is a strong ability of entanglement of individual nanotubes leading to formation of clusters. These clusters tend to become hard and make the MWCNTs lose their special properties. Moreover, the stability of nanofluid has not been assessed quantitatively in the studies made so far. Further the defects produced in MWCNTs due to ball milling and its consequential effects on tribological properties also need to be assessed. The present study is aimed at investigating improvements in antiwear, antifriction, and extreme pressure properties of formulated EP 140 grade gear engine oil dispersed with surface-modified and ball-milled MWCNTs. Ball milling is performed in inert gas medium and at a low intensity to prevent damage to the structure of MWCNTs. A simpler surface modification technique is used to stabilize the MWCNTs in oil medium and the stability of the suspensions is investigated over a period of 2 months. The effect of decrease in length of MWCNTs due to ball milling on the tribological properties has been studied. The repeatability of results over a period of 60 days is investigated to observe consistent performance and the average values are reported. The effect of additives in the oil along with surface-modified MWCNTs has resulted in use of lesser amount of MWCNTs in the lubricant dispersion compared to studies reported in the literature which is one of the novel features of the study. The paper also compares chemical and physical routes for dispersion of MWCNTs in lubricant by comparing performance of surface-modified pristine MWCNTs and surface-modified ball-milled MWCNTs, respectively.

2. Experimental

2.1. Materials. In the present study, multiwalled carbon nanotubes produced by CVD method have been procured from M/s Cheap Tubes Inc., USA. The size of MWCNTs is 20-40 nm in diameter, 25 microns in length, and 95% of purity. All other chemicals purchased are of GR grade. The surfactant is AR grade procured from M/s Sigma Aldrich India Pvt limited. GL4 (EP 140 grade) gear oil is selected as base lubricant.

2.2. Ball Milling of Multiwalled Carbon Nanotubes. As the length of the carbon nanotubes is thousands of times larger than their width, ball milling of MWCNTs is a common procedure to generate short and open-ended nanotubes. Ball milling apparatus consists of tungsten carbide lined bowls containing tungsten carbide lined ball. Arrangement is provided to perform ball milling under argon atmosphere to prevent oxidation of material during ball milling. The speed of rotation of bowls is set at 400 RPM and the ratio of balls to MWCNTs is taken as 10:1 to ensure minimal damage to the tubular structure of the MWCNTs. Higher speeds and ratios will increase the impact and thereby attrition of MWCNTs. Ball milling was performed for 4 and 20 hours at 400 RPM to avoid damage to the structure. After ball milling, the MWCNTs are heated in air at 600°C to remove amorphous carbon generated during ball milling process. These ball-milled MWCNTs are characterized using HRSEM and transmission electron microscopy to determine the average length of the MWCNTs.

2.3. Electron Microscopy. Figure 1(a) shows HRSEM image of pristine long length entangled MWCNTs. Figure 1(b) shows MWCNTs ball-milled for 5 hours with a small change in length of MWCNTs as compared to Figure 1(a). Figures 2(a) and 2(b) show images of 10- and 20-hour ball-milled MWCNTs.

It can be seen that the average length of 10-hour ball-milled MWCNTs is under 4 microns. From Figure 2(b) (TEM image) it can be observed that the length of 20-hour ball-milled CNTs has come down to around 150 nm size.

2.4. Raman Spectroscopy. Raman spectroscopy is employed to assess the formation of defects during ball millings and shown in Figure 3 for pristine MWCNTS, 5-, 10-, and 20-hour ball-milled MWCNTs. The sp2 structure of MWCNTs causes first order peaks D and G bands that are approximately located at 1350 cm^{-1} and 1580 cm^{-1}, respectively. Defect free MWCNTs due to intact hexagonal graphite structure make the G-band sharper. Defects in MWCNTs make the G-band peaks wider and shorter. On the other hand, D band peak represents lattice defects and finite crystal size. During defect

Table 1: Summary of research carried out by authors.

Authors	Base fluid, type of nano materials and concentration	Experimental apparatus	Major findings
Bhaumik et al. [6]	Mineral oil dispersed with graphite and MWCNTs in concentration 0.1 to 0.6 Wt%.	Pin on disk tribometer and Four-ball tester	It is found that MWCNTs outperformed graphite with wear reduced by 70-75% and load bearing capacity increasing by 20%.
Chen et. al. [5]	Paraffin oil dispersed with stearic acid modified MWCNTs in 0.45% Wt %	Ring on plate	Friction coefficient decreased by 10%, wear reduced by 30-40%. It was proposed that friction-reduction ability of nano-lubricant depends on both nano materials and obtaining stable dispersion of nano-particle in lubricant.
Cornelio et. al. [7]	Oil and water with SWCNTs & MWCNTs 0.01 to 0.05 Wt %	Twin-disk machine for measurements in rolling-sliding contact	The friction coefficients and wear losses measured were lower for either oil or water dispersed with nanotubes with friction coefficients reported as low as 0.063. It was proposed that decrease of friction and high wear resistance are due to the formation of an amorphous carbon film transferred from the CNT's on the surface.
Ghaednia et. al. [8]	Mineral base oil dispersed with CuO (9 nm) in 0.5 to 2 wt%	disk-on-disk friction and wear test	Friction coefficient decreased by 14 and 23% for the CuO nanoparticle concentrations of 1.0 and 2.0% wt, respectively. It was suggested that the reduction in the real area of contact due to dispersion of nanomaterials in lubricant is possible mechanism for reduction of friction
Hernandez Battez et. al. [9]	poly-alpha-olefin(PAO6) dispersed with CuO, ZnO and ZrO2 in 0.5 to 2% wt	Four-ball tester	The results indicate that the extreme pressure behavior of lubricant with nano particles is strongly dependent on the size and hardness of the nanoparticles. Particles with hardness less than surfaces in contact exhibited good EP behavior.
Hu et. al. [10]	Water dispersed with sodium dodecyl sulfate modified oxidized MWCNTs in 0.1% Wt (for application in metal working fluids)	Four-ball tester	It is found that oxidation of MWCNTs produced defects on the surface leading to formation of better suspension. There is a good improvement in tribological properties with surfactant modified MWCNTs compared to pristine MWCNTs indicating strong influence of stability of suspension.
Joly-Pottuz et. al.[11]	poly-alpha-olefin dispersed with carbon nano onions and graphite powders in 0.1% wt	pin-on-flat tribometer	Carbon nano-onions show better tribological properties than graphite powder. It is also found that tribofilm formed by carbon onions converts wear particles into ultrafine lubricious iron oxides, thus preventing further abrasive wear process.
Khalil et. al. [12]	Mobil gear 627 and paraffinic mineral oils in 0.1 to 2 wt%	Four-ball tribotester	A 50% reduction in friction and an increase in weld load by up to 100% are observed with dispersion of MWCNTs in lubricant. The Tribological performance is attributed to deposition of MWCNTs nanoparticles on the worn surface resulting in decreasing the shearing stress, thus improving the tribological properties.
Lee et. al. [13]	Raw mineral oil (Sun Oil, Japan) dispersed with fullerenes in 0.01 to 0.05% wt.	disk-on-disk tribotester	Fullerenes have reduced friction by 30% by reducing the metal surface contacts. Further, it is found that volume fraction is a key factor to control the friction and wear
Lee et. al. [14]	Commercial gear oil dispersed with nano graphite (55 nm) in 0.1 to 0.5% wt. Alkyl aryl sulfonate is used as dispersant	disk-on-disk tribotester	The results indicate dispersion of nano graphite in lubricant boosted the lubrication characteristics. The possible reason for improvement of properties is suggested to be due to nanoparticles acting as ball bearing spacers between the friction surfaces reducing the contact between the plates.

Table 1: Continued.

Authors	Base fluid, type of nano materials and concentration	Experimental apparatus	Major findings
Pena-Paras et. al. [15]	4 types of Metal working fluids dispersed with TiO_2, Al_2O_3, CuO and MWCNTs in 0.01 to 0.1% wt	A four-ball T-02U tribotester	All nano materials improved the tribological properties with MWCNTs giving best results. Tribo-sintering of nano materials on the rubbing surfaces during machining is the reason proposed for the performance improvement.
Puzyr et. al. [16]	Commercial oil dispersed with surface modified nano diamonds in 0.01% wt	block-on-ring test setup	Nano diamond additives in oils improved the anti- wear properties and decreased the oil temperature compared to base oils. The anti-wear mechanism of ND additives was attributed to the formation of a hard and porous layer between the contact surfaces.
Sarma et. al. [17]	SM grade engine oil dispersed with Cu and TiO2 nano particles in 0.025 to 0.1% wt	Pin on disk tester and engine test rig	It was found that copper nano particle dispersed lubricant gave best results on engine tests. 3 to 5% increase in thermal efficiency of the engine is observed.
Srinivas et. al. [18]	EP 140 Transmission oil dispersed with WS_2 and MoS_2 nano materials in 0.5% wt.	Four-ball tester	Lubricant dispersed with WS_2 nanoparticles gave higher weld load and load wear index (LWI) than that of lubricant dispersed with MoS_2 nanoparticles. The reason for better performance of WS_2 nano particles is attributed to their lower hardness resulting in better deposition on the rubbing surfaces under load.
Srinivas et.al. [19]	CI 4 Engine oil dispersed with long MWCNTs	Four-ball tester	The surface modification of multi walled carbon tubes plays prominent role in the improving stability and thereby anti-wear and anti-friction properties of engine oils.
Viesca et. al. [20]	Poly alpha olefin (PAO6) dispersed with carbon coated nano particles in 0.5 to 2% wt	Block on-ring tribometer and four-ball tester	carbon-coated copper nanoparticles decreases wear and increases the load-carrying capacity of polyalphaolefin

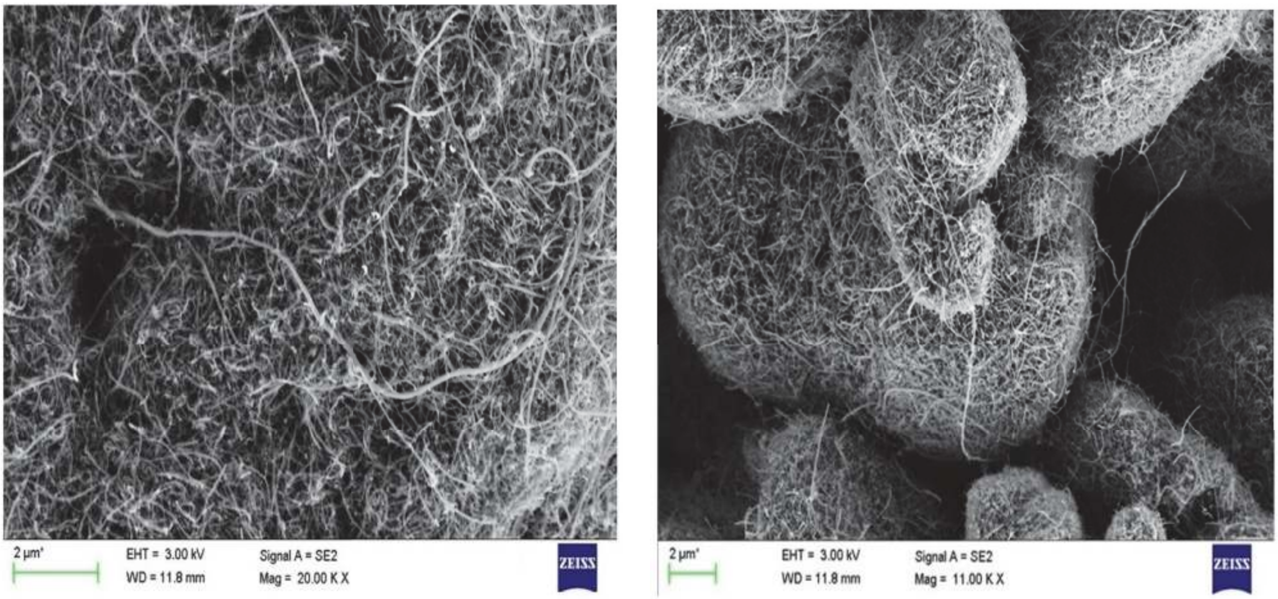
Table 2: Raman Spectra characteristics of MWCNTs.

MWCNTs	Intensity of D band, ID	Intensity of G band, IG	Intensity of G' band, IG'	Ratio of ID and IG
Pristine	1536	2100	1594	0.731
5 hour ball milled	1261	1708	1082	0.738
10 hour ball milled	1410	1855	974	0.76
20 hour ball milled	1413	1266	774	1.11

formation, due to breaking of the 2D translational symmetry the D band peak will increase and become wider. Another peak G' band which can be seen at 2700 cm^{-1} Raman Shift represents amorphous defects in MWCNTs.

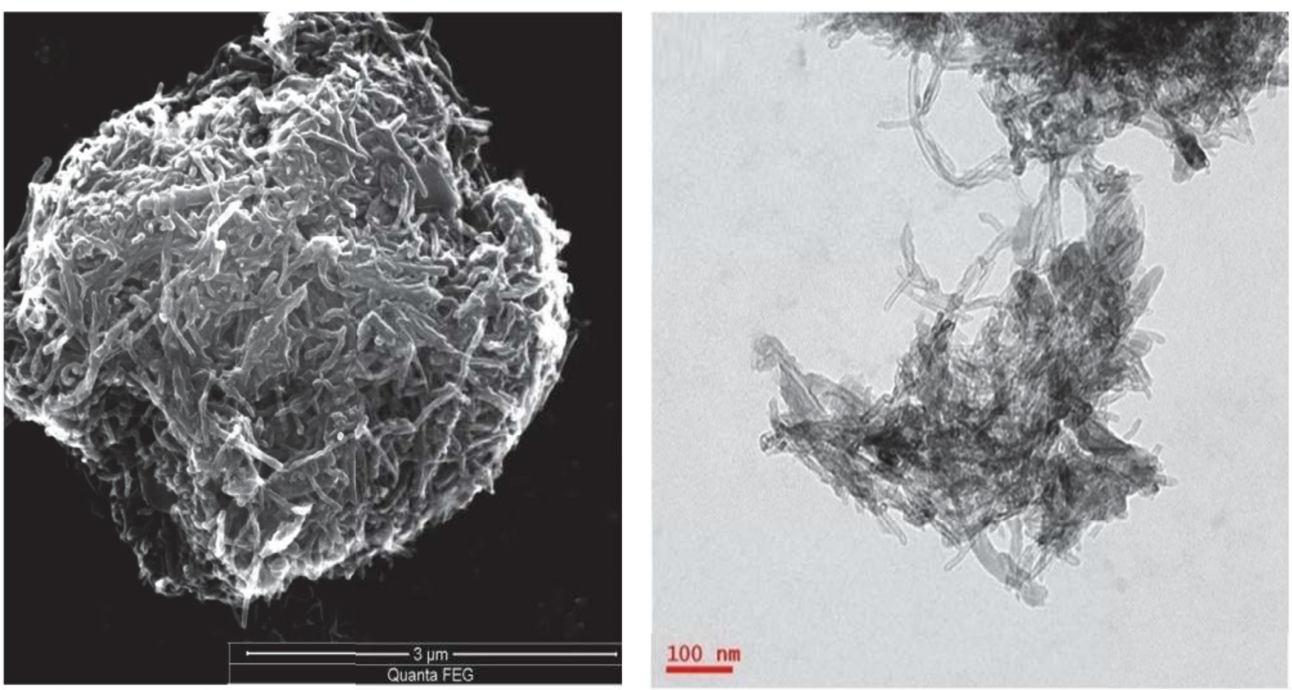
Table 2, provides the intensities of D, G, and G' bands. In case of pristine MWCNTs, 5- and 10-hour ball-milled MWCNTs, there is no significant difference in the intensities of D, G, and G' bands with ratio of intensities of D and G bands remaining marginally the same. In case of 20-hour ball-milled MWCNTs, a significant decrease in intensity of G and G' bands is observed with increase of intensity of D band indicating mild destruction of graphite structure and formation of amorphous defects. In all cases, the peaks of all bands are sharp indicating either no defects or mild defect (in case of 20-hour ball-milled MWCNTs).

2.5. Surface Modification of MWCNTs. Pristine MWCNTs tend to agglomerate and form large particles clusters in liquid medium. Moreover, after the ball milling process, the MWCNTs tend to be compressed by the balls forming larger aggregates of entangled MWCNTs. To disentangle them and make them stable in the lubricant medium, it is required to modify the surface of MWCNTs with a surfactant to create stearic repulsions between individual nanotubes. To stabilize the nanoparticles in the liquid medium, a surfactant SPAN 80 (Sorbitan monooleate) is used to modify surface of MWCNTs during the preparation of oil. SPAN 80 is a nonionic surfactant with a hydrophilic-lipophilic balance of 4.6 which is ideally suitable for oils. It adsorbs on the surface of MWCNTs reducing their surface energy, thereby preventing agglomeration



(a) (b)

Figure 1: HRSEM images of pristine and 5-hour ball-milled MWCNTS. (a) Pristine MWCNTS, (b) 5-hour ball-milled MWCNTS.



(a) (b)

Figure 2: HRSEM images of 10-hour and 20-hour ball-milled MWCNTs. (a) 10-Hour ball-milled MWCNTs, (b) 20-hour ball-milled MWCNTs.

and settling of nanoparticles. To prepare surface-modified MWCNTs, SPAN 80 and multiwalled carbon nanotubes (both pristine and ball-milled) are taken in the ratio of 2:1 and ultrasonicated in a solvent for 30 minutes, which creates a mechanochemical reaction. This reaction coats the surfactant on to the surface of the MWCNTs.

2.6. FTIR Spectroscopy. The surface-modified MWCNTs are characterized for functional groups on the surface using

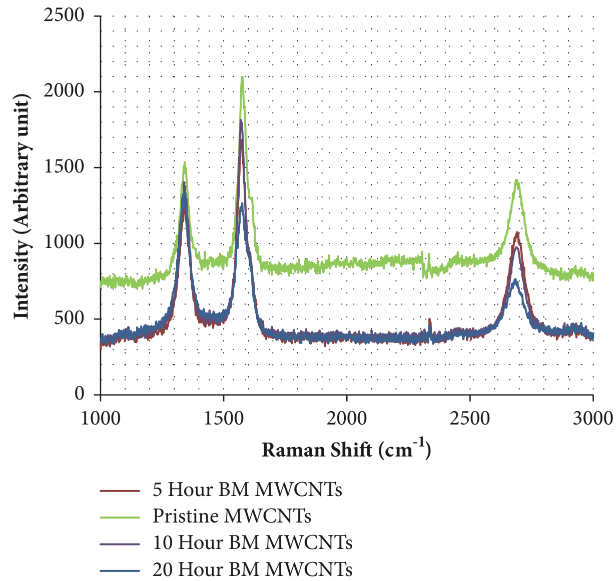


Figure 3: Raman spectroscopy of pristine and ball-milled MWCNTs.

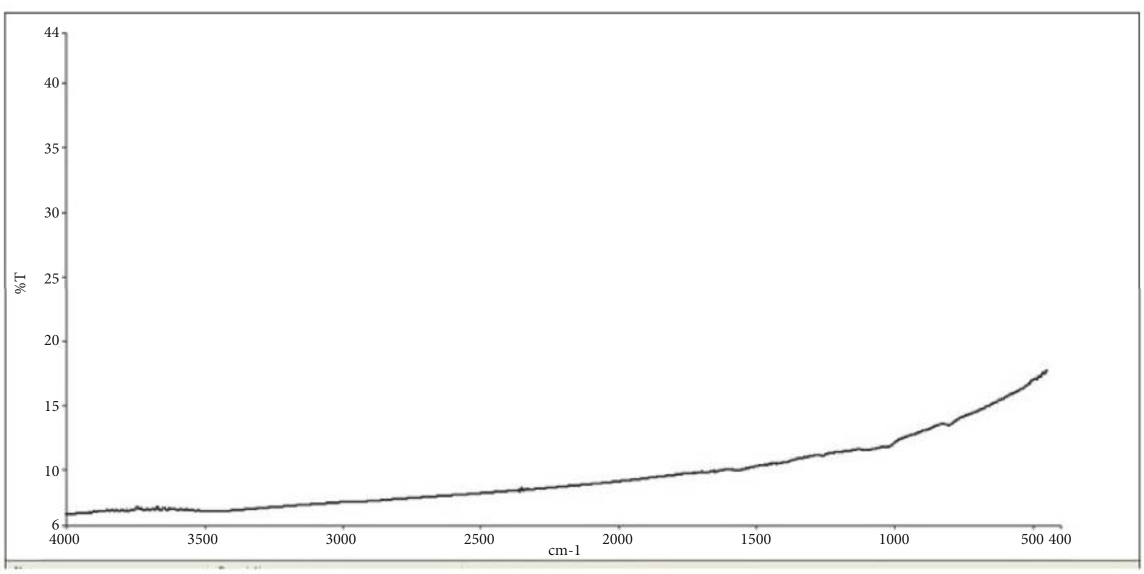


Figure 4: FTIR spectroscopy of pristine MWCNTs.

Fourier transforms infrared spectroscopy as shown in Figures 4 and 5. Figure 4 shows pristine MWCNTs with no characteristic peak detected. Figure 4 shows the FTIR image of surface-modified MWCNTs with characteristics peaks between 1463 and 1486 cm^{-1} wavelength indicating lipophilic groups attached to the surface.

2.7. Preparation and Evaluation of Stability of Lubricants with MWCNTs. The surface-modified long and ball-milled MWCNTs in 0.5 weight percent are dispersed in lubricating oil by processing it in a probe ultrasonicator (**Hielscher UP400S)** for about 30 minutes. The stability of the nanofluid for a period of 60 days is monitored by light scattering techniques. Ball-milled MWCNTs when dispersed in lubricating oils could form better stable suspension compared to long MWCNTs and gave better tribological properties.

The stability of the lubricants dispersed with MWCNTs is evaluated using light scattering techniques by means of zeta sizer (Horiba SZ 100). The zeta potential of the samples, an indicator of dispersion stability of MWCNTs in the lubricating oil medium, has been analyzed over a period of 60 days. A zeta potential value of ± 40 indicates good stability. As the viscosity of the gear oil is high, the oil samples are diluted using toluene before charging it into the zeta sizer to improve the transmittance of the oil so that accurate values

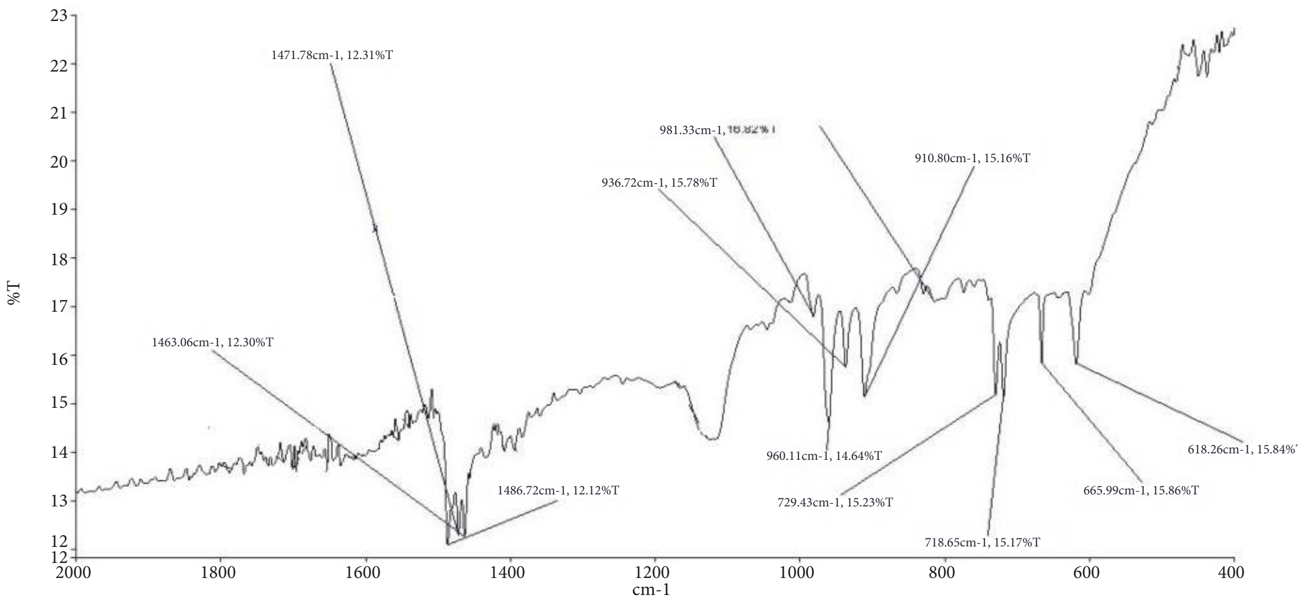
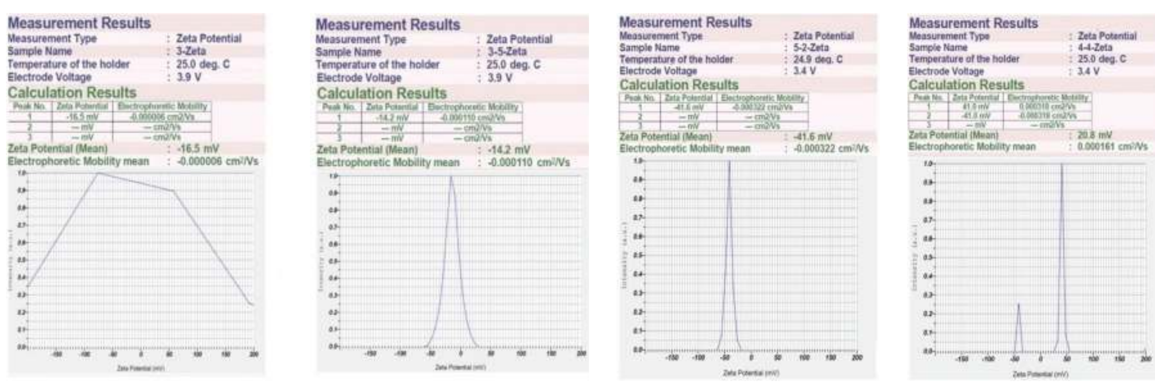


Figure 5: FTIR spectroscopy of surface-modified MWCNTs.



(a) (b) (c) (d)

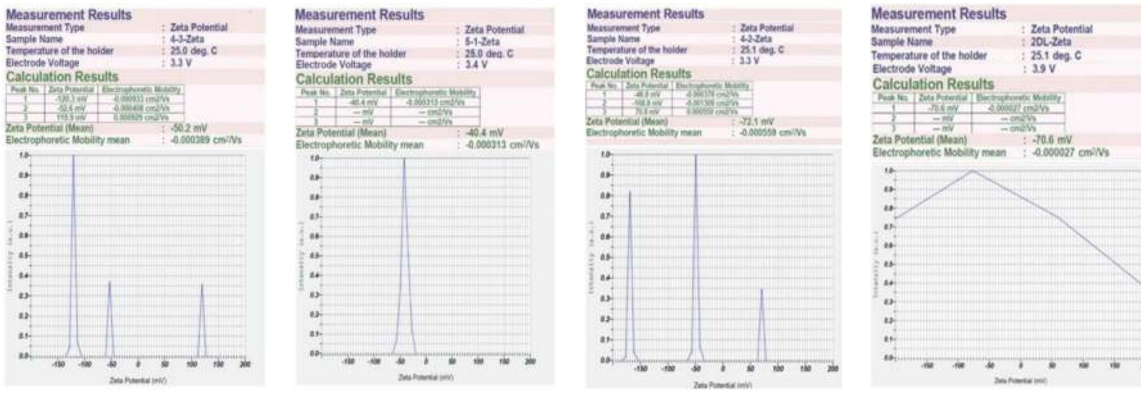
Figure 6: Zeta potential variation of nanofluids during 60 days. (a) Lubricants with long MWCNTs immediately after preparation, (b) lubricant with long MWCNTs after 60 days, (c) lubricant with 5-hour ball-milled MWCNTs immediately after preparation, (d) lubricant with 5-hour ball-milled MWCNTs after 60 days.

can be obtained. Higher values of zeta potential values are found when the oil samples are dispersed with ball-milled MWCNTs. The variation of zeta potential immediately after preparation and 60 days after preparation is shown in Figures 6 and 7.

Figures 6(a) and 6(b) show the variation of zeta potential of lubricant dispersed with long MWCNTs and 5-hour ball-milled MWCNTs, respectively. As can be seen the zeta potential with long MWCNTs is much less indicating low stability. With five-hour ball-milled MWCNTs there is an improvement in the stability compared to stability of long MWCNTs. Figures 7(a) and 7(b) show the variation of zeta potential of lubricant dispersed with 10-hour and 20-hour ball-milled MWCNTs. As can be seen there is a significant improvement in the stability with 20-hour MWCNTs showing best stability. This can be attributed to lower agglomeration rates due to short length of MWCNTs.

2.8. Physicochemical Properties of Test Oils. The gear oils are manufactured by blending base stocks and additive components to meet the requirements of standards. Basic physicochemical properties should be in compliance with international standards for statutory purposes. The main physicochemical properties to be assessed for a gear oil are viscosity, viscosity index, pour point, flash point, total acid number, and copper strip corrosion resistance. All the properties for test oils are evaluated in 5 replicable experiments and the average values are reported.

As can be observed from Table 3, the effect of ball milling and surface modification has practically no effect on the



(a) (b) (c) (d)

Figure 7: Zeta potential variation of nanofluids. (a) Lubricants with 10-hour ball-milled MWCNTs immediately after preparation, (b) lubricant with 10-hour ball-milled MWCNTs after 60 days, (c) lubricant with 20-hour ball-milled MWCNTs immediately after preparation, (d) lubricant with 20-hour ball-milled MWCNTs after 60 days.

physicochemical properties of the test oils. The viscosity and viscosity index are unchanged with dispersion of nanomaterials. Surface modification has no effect on pour point, flash point, and total acid number of the test lubricants.

2.9. Tests for Tribological Properties. The test oils are tested for improvement in tribological properties on a four-ball tester. The weight percentage of surface-modified and ball-milled MWCNTs is maintained as 0.5 wt %. The standard code of the tests, a rotating steel ball, is pressed against three steel balls firmly held together under a load and immersed in lubricant. The test parameters of load, duration, temperature, and rotational speed are set in accordance with standard test procedure.

In wear test done as per ASTM D 4172, the average scar diameter formed on the bottom of three balls shows the ability of the lubricant to prevent wear. A larger diameter indicates poor antiwear behavior. The test is carried out for one hour at a load of 40 kgf and speed of 1200 RPM with temperature of oil maintained at 75°C.

The friction test is carried out to find the friction coefficient offered by the lubricant as per ASTM D 5183 code. Initially the balls are subjected to "wear in" for one hour at a load of 40 kgf and speed of 600 RPM with temperature of oil maintained at 75°C. After "wear in", the used lubricating oil is discarded and balls are cleaned. Fresh lubricant sample is taken in the ball cup with the same worn test balls in place. The test is again started under the above conditions with load varying from an initial load of 10 kgf and increasing by 10 kgf at the end of each successive 10 min interval until there is a sharp rise in the Frictional Torque which indicates incipient seizure. This is called seizure load which is an important factor in determining the effectiveness of the lubricant.

ASTM D 2783 specifies the extreme pressure properties of lubricant in terms of weld load which is the ultimate load at which the lubricant evaporates due to high pressure and temperature resulting in all the four balls welded to each other. The standard also specifies another parameter called "load wear index" which indicates the behavior of lubricant in resisting the aforementioned weld conditions. The test is used to determine the load carrying properties of a lubricant at high test loads usually encountered in gears. In this test on four-ball tester a series of 10 tests of 10-second duration are carried with varying load under the following conditions:

temperature of oil: room temperature,

speed of rotation: 1760 RPM,

duration: 10 s,

load applied: 32 kgf to weld load.

A total of 10 readings are considered in the test and the corrected load is calculated for all ten readings. The load wear index is a single parameter that shows the overall EP behavior in a range between well below seizure and welding is calculated from the corrected load.

$$\text{Corrected load} = \frac{\mathrm{LD_H}}{\mathrm{X}} \quad (1)$$

where L is the applied load, kgf, X is the average scar diameter on the worn balls in mm and Hertz scar diameter, and $D_H = 8.73 \times 10^{-2}(\mathrm{L})^{1/3}$ in mm. The load wear index is calculated from the expression LWI = (A/10) (kgf), where A is the sum of the corrected loads determined for the ten applied loads immediately preceding the weld load.

3. Results and Analysis

All the tests are conducted in ten repeatable trails over a period of 60 days to ascertain the influence of nanoparticles in terms of repeatable and reproducible results, and the average values are reported. The results of wear test conducted as per ASTM D4172 are as given below for different test oils. From Table 4, it can be observed that the average wear scar of lubricant with MWCNTs is much less than that of base lubricant. Further, with dispersion of long MWCNTs, the range of wear scar over 60 days of testing is higher compared to other oils due to poor lubricant suspension.

Table 5 shows the results of friction test in terms of average friction coefficient and seizure load. With dispersion

Table 3: Physicochemical properties of test oils.

Test oil	Viscosity at 40°C (cSt)	Viscosity at 100°C (cSt)	Viscosity index	Flash Point °C	Pour Point °C	Total Acid Number (mg KOH/g)	Copper strip Corrosion test
Base oil (EP140 gear oil)	408.4	27.9	94	194	-3	0.25	2a
Base oil +0.5% pristine MWCNTs	409.1	27.75	93	192	-3	0.26	2a
Base oil + 0.5% 10 hour ball milled MWCNTs	410.2	28.6	95	194	-3	0.25	2a
Base oil + 0.5% 20 hour ball milled MWCNTs	411.5	28.4	95	194	-3	0.26	2a

Table 4: Results of wear test conducted as per ASTM D 4172 at 40 kgf load.

Test Oils	Average wear scar in microns
Base lubricant (EP 140 transmission oil)	352.353
Base lubricant + long MWCNTs	347.071
Base lubricant + 5 hour Ball milled MWCNTs	335.085
Base lubricant + 10 hour Ball milled MWCNTs	317.954
Base lubricant + 20 hour Ball milled MWCNTs	323.547

Table 5: Results of friction test conducted as per ASTM D 5183.

Test oil	seizure load, kgf	Average coefficient of friction
Base lubricant (EP 140 transmission oil)	220	0.0901
Base lubricant + long MWCNTs	230	0.0839
Base lubricant +5 hour Ball milled MWCNTs	240	0.0784
Base lubricant + 10 hour Ball milled MWCNTs	260	0.0746
Base lubricant + 20 hour Ball milled MWCNTs	240	0.0783

of ball-milled MWCNTs, there is a good improvement in both seizure load and the friction coefficient.

The 10 sets of results of repeatable friction characteristics are plotted in graphs in Figure 8. In case of lubricant dispersed with long MWCNTs, although the performance improved during the initial days, there is steady decrease in the performance characterized by increase in friction coefficient due to poor stability over a period of time. Shortened MWCNTs due to their better stability gave a consistence performance over a period of 60 days with lubricant dispersed 10-hour ball-milled MWCNTs giving best performance. The variation of friction torque with time is plotted in Figure 9. From the graph it can be seen that the effect of nanomaterials is more significant at higher loads. In boundary lubrication regime there is significant contact between surfaces separated by a thin lubricant film. Increase of normal load would sweep the lubricant out of the contact region, reducing the lubricant film thickness between surfaces and increasing the chance of contact between surfaces in motion. Due to short length, the ball-milled MWNTs dispersed in lubricant could effortlessly glide and roll between the two contact surfaces in motion like spacers. This increases the pressure limits of the lubricant, thereby significantly reducing friction coefficient and improving the seizure load. Lubricant dispersed with ball-milled MWCNTs has shown consistent performance on the torque-time plot compared to base lubricant.

The extreme pressure properties, namely, last nonseizure load, weld load, and load wear index of test oils under consideration, are summarized in Table 6.

With dispersion of MWCNTs, there is an improvement in last nonseizure load, weld load, and load wear index. A graph showing the variation of wear scar diameter with load is shown in Figure 10. The region between points 0 to 1 is normally designated as antiwear region in which all the lubricants exhibited similar behavior. Points 1 and 1′ indicated the last nonseizure load (LNSL) up to which the wear scar formed is uniform.

The region above last nonseizure load is called extreme pressure zone in which the efficacy of additives in the gear oil comes into play. In this region, the pressures and temperature are very high and the additives are supposed to withstand these extremities. MWCNTs due to their good mechanical properties could form a barrier between the surfaces withstanding the extremities to improve weld load.

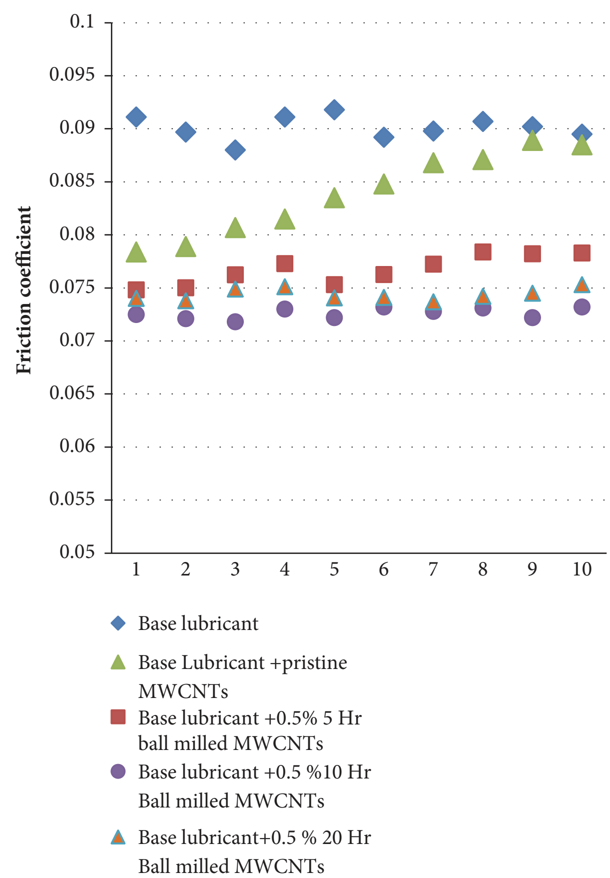


Figure 8: Variation of friction coefficient in 10 repeatable tests carried out during 2 months.

Table 6: Results of EP test conducted as per ASTM D 2783.

Test oil	Last non seizure load, kgf	weld load, kgf	load wear index
Base lubricant (EP 140 transmission oil)	120	250	64.82
Base lubricant + long MWCNTs	120	315	69.54
Base lubricant +5 hour Ball milled MWCNTs	140	315	71.23
Base lubricant + 10 hour Ball milled MWCNTs	140	400	75.65
Base lubricant +20 hour Ball milled MWCNTs	120	250	72.81

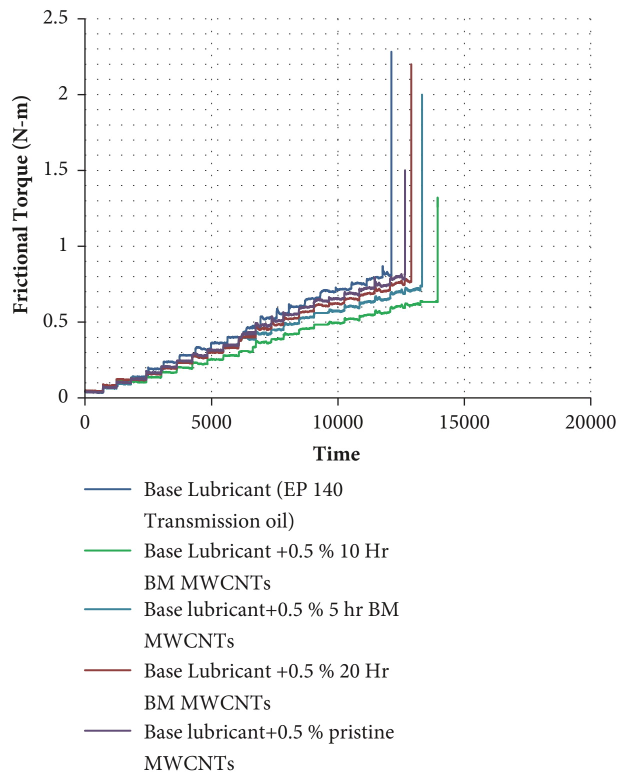


Figure 9: Variation of friction torque with time during friction test.

There is a reduction in the wear scar with dispersion of pristine and ball-milled MWCNTs. The effect of dispersion of shortened MWCNTs is found to be quite visible in this region. Lubricant dispersed with 10-hour ball-milled MWCNTs improved the LNSL and could reduce the wear scars even in the extreme pressure regions. Lubricant dispersed with ball-milled MWCNTs due to decrease of the friction coefficient offered lower wear scars on the test balls. Further after last nonseizure load, it can be observed that the wear scar diameter with dispersion of nanomaterials is significantly low, resulting in improvement in load wear index as well as weld load. This is due to better dispersion owing to short length. Here the ball milling timing of MWCNTs plays an important role in defining the optimum length with minimum damage to the tube structure. The optimum length for attaining good stability and tribological properties can be assessed as 1 to 5 microns, which can be attained with 10 hours of ball milling at 400 RPM speed. 20-hour ball-milled MWCNTs could improve the load wear index by performing well in the antiwear region but, due to defect formation during ball milling, exhibited lower performance in EP region. This can be attributed to the formation of defects on the surface (Figure 3 and Table 2) leading to loss of special properties of MWCNTs.

4. Conclusions

(1) The ball milling of multiwalled carbon tubes prior to dispersion in lubricant plays an important role in improvement of stability, antiwear, antifriction, and extreme pressure properties of gear oil.

(2) Ball milling could shorten the MWCNTs making them stable in the lubricant for a period of more than 60 days.

(3) From Raman spectroscopy it can be observed that ball milling time of up to 10 hours did not produce any defects on the surface of MWCNTs but 20-hour ball milling produced mild defects on the surface.

(4) Long MWCNTs, although surface-modified, when dispersed in lubricants exhibited poor stability and could

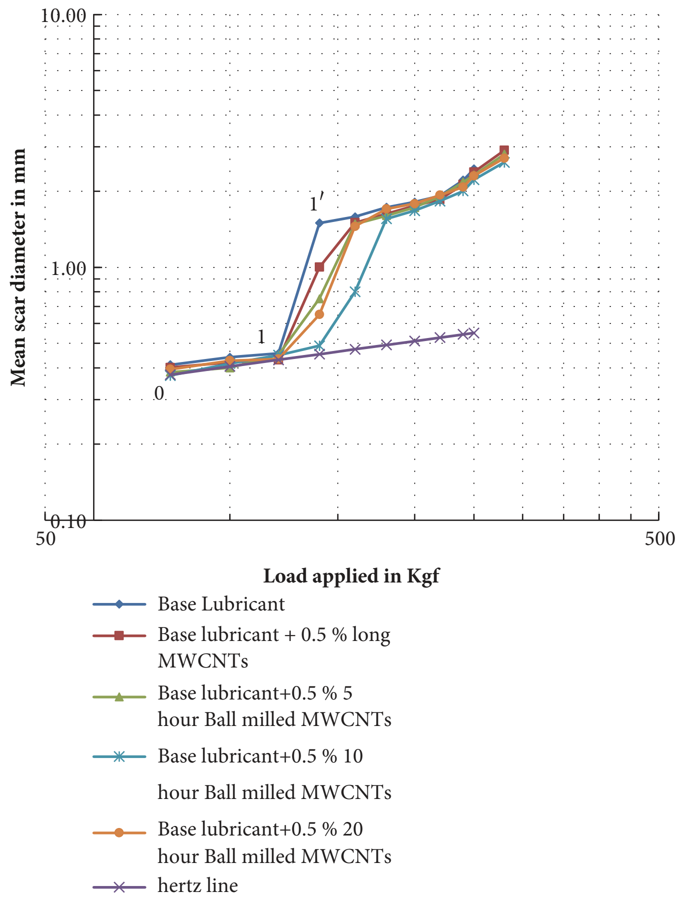


Figure 10: Variation of wear scar diameter with applied load during EP test.

marginally improve the antifriction and extreme pressure properties.

(5) The physicochemical properties remain unaltered with dispersion of surface-modified and ball-milled MWCNTs.

(6) There is a good improvement in the wear scar diameters and friction coefficients with dispersion of shortened MWCNTs as short-length MWCNTs could slide between mating surfaces reducing contact.

(7) The load wear index and weld load of lubricants dispersed with shortened MWCNTs have improved significantly as the performance of short MWCNTs is good in both antiwear and extreme pressure region.

(8) At an optimum length of MWCNTs in the range of 1 to 3 microns, the lubricant could give best results while too short MWCNTs due to formation of defects despite forming good suspension could not give best performance.

Nomenclature

D_H: Hertz scar diameter
EP: Extreme pressure
AW: Antiwear
L: Load applied
LNSL: Last nonseizure load
LWI: Load wear index
MWCNTs: Multiwalled carbon nanotubes
SL: Seizure load
X: Average scar diameter.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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