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Influence of Size and Weight Fraction of Multi-Walled Carbon Nanotubes Dispersed in Gear Oils for Improvement of Tribological Properties

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Keywords: Ball-milling, Multi-wall carbon nanotubes (MWCNTs), Defects on MWCNTs, Gear oil, Raman spectroscopy, Surface modification, Tribological properties

ABSTRACT

The paper investigates the effect of size, and weight fraction of multi-walled carbon nanotubes (MWCNTs) dispersed as an additive in the gear oil to enhance the tribological properties. The method of modifying the surface of multi-walled carbon nanotubes with a surface modifying agent before mixing in the oil improved dispersion stability. Studies were carried out to evaluate the size and shape of MWCNTs before and after ball-milling. The electron microscopy and Raman spectroscopy are used to characterize the nanotubes.

The pristine long nanotubes and ball-milled nanotubes are mixed in EP 140 gear oil in 0.25, 0.5& 1.0 weight per cent and the stability of the oils measured using light scattering techniques. The anti-wear, anti-friction and extreme pressure properties of oils dispersed with nanotubes were tested on a four-ball wear tester. Using Raman spectroscopy, it was identified that ball-milling for ten hours didn't create any flaws on the periphery of Multi-wall carbon nanotubes. Ball-milling for prolonged time resulted in the formation of defects on the surface of MWCNTs, thereby lowering their advantage as oil additives. The stability of the oil and the anti-wear, anti-friction and extreme-pressure properties have considerably enhanced with the dispersion of short MWCNTs. It is found that length and weight per cent of MWCNTs strongly impact the stability, anti-wear and anti-friction properties of the oil. Further, the Multi-wall carbon nanotubes loading in oil beyond certain weight fraction results in deterioration of properties. Shortening of nanotubes resulted in the use of lower weight fractions for the enhancement of tribological properties.

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INTRODUCTION

The Gear oils are generally used to reduce the wear and friction between the rubbing surfaces and to protect the components from pressures and higher impacts. The gear oils are added with anti-wear (AW)and extreme-pressure (EP) additives to withstand for excessive pressure and temperatures. These additives react chemically with the metal surfaces, forming easily sheared layers and thereby preventing severe wear and seizure. Many researchers have done experiments on different nanoparticles as additives to increase tribological properties. In recent days, due to the unique features of the allotropes of carbon such as graphene, graphite fullerenes and carbon nanotubes (CNTs), researcher have shown much interest in this particular area.CNTs possess excellent mechanical properties due to sharp *sp*2 C–C bond of CNTs and when dispersed in enhancing the features. The strong *sp*2 C–C bond in the carbon nanotubes (CNTs) helps in exponentially improving mechanical properties, and their dispersion in oils improves tribological properties. Carbon nanotubes are of three grades, namely, single-walled carbon nanotubes, double-walled carbon nanotubes and multi-walled carbon nanotubes (MWCNTs). The surface modification of the Multi-wall carbon nanotubes is simple owing to their large surface area compared to many inorganic nanomaterials. The dispersion of the Multiwall carbon nanotubes in the oil itself is an enormous task, and many researchers have conducted novel studies on the effect of dispersion in oils to improve anti-wear and anti-friction properties. The aspect ratio of the carbon nanotubes is very high because of which the carbon nanotubes entangle with each other to form agglomerates which are the main challenge to obtain stable suspension in the liquid medium.

There are several methods to reduce the length of the carbon nanotubes proposed by many researchers. One of the best ways to reduce the length of the nanotubes is by ball-milling without damage to the shape and structure and to maintain open ends. However, excessive ball-milling of nanotubes may produce defects and damage the graphite structure, making them useless for dispersion in oils. Dresselhauset et al. (2010) and Paton et al. (2014) studied the methods of identifying the surface defects and purity of carbon nanotubes and graphene. In their studies, they proposed that the purity and the defect density of carbon nanotubes depend on the intensity of G-band and the D/G ratio. Pierard et.al. (2004)have investigated the surface defects and structure of single-walled carbon nanotubes after ball-milling. In their studies, they employed Raman spectroscopy to study the surface defects formed in ball-milling at different time intervals and revealed the optimum time for ball-milling without any abnormalities to the tubular structure. The time of over 50 hours of ball-milling of single-walled carbon nanotubes destroyed the structure producing amorphous carbon.

Different studies were conducted on gear oils for the enhancement of tribological properties with dispersion MWCNTs. The results of the reviews give a clear picture that the tribological features wear, and friction characteristics of oil depend on the nanomaterial used as an additive and the stability of the nanoparticles in oils. Chen et al. (2005) studied the stability and enhancement of properties of liquid paraffin oil dispersed with ball-milled and stearic acid-modified Multiwall carbon nanotubes (MWCNTs). The tribological tests were conducted on a pin-on-plate wear-testing machine. It is identified that the stability of the ball-milled MWCNTs dispersed in oil, the anti-wear and anti-friction properties have improved. It was also concluded that the coefficient of friction decreased by 11 %, whereas the wear reduced by 30-40%.

Bhaumik et al. (2014) conducted experiments on oil dispersed with graphite and Multi-wall carbon nanotubes in concentrations of 0.1 to 0.6 weight per cent. They did tests on a pin on disk tribometer, and Fourball wear tester. The test results show that the Multi-wall carbon nanotubes have enhanced the oil properties with wear decreased by 70-75 % along with an increase in load-bearing capacity by twenty per cent. Pena-Paras et al. (2014) studied tribological properties of TiO_2, Al_2O_3, CuO and MWCNTs with weight % of 0.01 to 0.1 % in 4 different types of Metalworking fluids. It was identified that aluminium nanomaterials had increased the tribological properties where MWCNTs gave the best results among the 4 nanomaterials. Tribo-sintering of nanoparticles on the rubbing surfaces during machining was the reason proposed for the enhancement of performance.

Summary of the prior art

Most of the studies above investigated the effect of dispersion of higher quantity of MWCNTs in base oils or paraffin oils resulting drastic increase in the viscosity of the oil, thereby enhancing the tribological properties. Moreover, the effect of concentration of MWCNTs on the tribological properties and the stability of nanofluid has not been evaluated quantitatively in these studies. Further, the impact of the size of dispersed MWCNTs on the stability of oil and tribological properties also needs investigation.

Present studies

The present research aims at exploring enhanced extreme-pressure, anti-friction, and anti-wear properties of surface-modified and shortened MWCNTs dispersed in EP 140-grade gear oil. The Multi-walled carbon nanotubes are ball-milled to reduce the length of the tubes and impact of shortening on weight fraction of MWCNTs for the property enhancement is investigated. Ball-milling is done in a low-intensity inert gas environment to avoid destruction to the structure of MWCNTs. The effect ball-milling time on the length of MWCNTs and defect formation on their composition are essential to enhance tribological properties. In addition to the outcome of dispersion of ball-milled MWCNTs, the influence of weight fraction of dispersed MWCNTs on tribological properties is also investigated. Additionally, the defects created in MWCNTs due to ball-milling and its far-reaching consequences on tribological properties have also been judged. The effect of additives in the oil along with the dispersion of surface-modified short MWCNTs has ensured the use of the lesser amount of MWCNTs contrary to the findings stated in the literature which is one of the new aspects of the study.

EXPERIMENTAL PROCEDURE

Materials procurement

In the investigation, MWCNTs manufactured by chemical vapour deposition has been purchased from M/s Cheaptubes Inc., USA. The diameter range of MWCNTs is 30-40 nm, 25-micrometre length, and 99 % purity. All the chemicals and surfactant areAR grade purchased from M/s Sigma Aldrich India Pvt Ltd. commercial gear oil GL4 (EP 140 grade) is selected as base oil.

Ball-milling of Multiwalled carbon nanotubes

Carbon nanotubes have a longer length, compared to their diameter. Ball-milling is an economical method to shorten the long tubes of MWCNTs and make them short and open-ended. In the Ball-milling equipment, the bowls are internally coated with tungsten carbide lining, and the tungsten carbide balls are used. To prevent oxidation inert gas environment is provided by using argon gas throughout the milling. The weight of balls to the material is taken as 10:1, and the ball-mill bowls are rotated at 400 RPM ensuring no erosion to the tubular structure of the MWCNTs as greater rotational speeds and a higher ratio of balls to the material would result in more impact and thereby erosion of structure of MWCNTs. Ball-milling was conducted at different time durations ranging from five and twenty hours at 400 RPM to check the effect of the time on length and structure of MWCNTs. Since ball-milling produces amorphous carbon during processing, the processed MWCNTs are sintered in air at 600 ºC to remove amorphous carbon.HRSEM and transmission electron microscopy (TEM) were used to characterize ball-milled MWCNTs to assess the average length of the MWCNTs.

Electron microscopy

"Figure. 1a" depicts the image of pristine long MWCNTs taken in HRSEM. Five-hour ball-milled MWCNTs are shown in Fig 1b, and the change in length of MWCNTs can be observed when compared with pristine MWCNTs. Figs. 2a&2b illustrate images of ten and twenty-hours ball-milled MWCNTs, and it can be perceived that the average lengths of ten and twenty hours ball-milled MWCNTs are in the range of 0.15 – 6 microns.

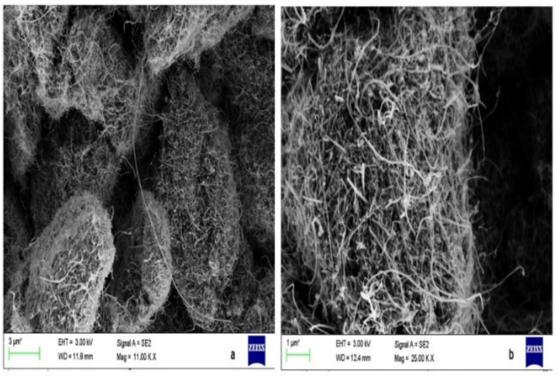

Fig. 1 HRSEM images of a) Pristine MWCNTs b) five hour ball-milled MWCNTs

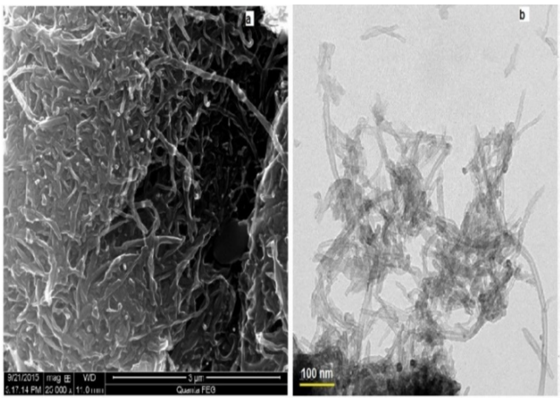

Fig. 2 HRSEM images of a) ten-hour ball-milled MWCNTs b) twenty-hour ball-milled MWCNTs

It can also be observed in Fig. 2b (TEM image) that after twenty hours ball-milling, the MWCNTs are extremely crushed and flawed due to high ball-milling impact.

Raman Spectroscopy

To assess the damage done to MWCNTs due to ball-milling, Raman spectroscopy was used to investigate the defects developed in the tubular structure. In Raman spectroscopy, the sp2 structure of MWCNTs creates first-order peaks of D and G located between 1250 $cm^{-1}$and 1600 $cm^{-1,}$ respectively. The defects created on MWCNTs produce wider and shorter G band peaks. Lattice defects and excellent crystal size can be assessed by D band peak. Defect formation on MWCNTs makes the D band to a height more and make it wider. Amorphous defects in MWCNTs are depicted by G′ group has seen at 2750 cm^{-1} Raman Shift.

The Raman spectrum for pristine long length MWCNTs five, ten and twenty hours ball-milled MWCNTs is shown Fig. 3. As can be seen from Fig. 3(a), Pristine MWCNTs are free from defect and intact hexagonal graphitic structure can be characterized by a sharp G band. In the case of five and ten-hours ball-milled MWCNTs the spectrum, as shown in Fig. 3(b) and Fig. 3(c) is similar to pristine MWCNTs with negligible changes in the intensities of D, G, and G’ bands. The ratio of D and G bands intensities remained similar for pristine, five hours ball-milled and ten hours ball-milled MWCNTs. For the case of twenty hours ball-milled MWCNTs, a significant drop in the G and G’ bands intensity is observed with D band peak intensity increasing which shows light damage to the graphite structure and creation of amorphous defects. Table 1, provides the strengths of the D, G and the G’ bands.

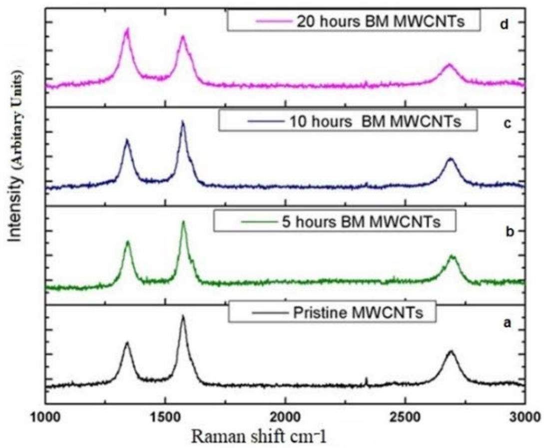

Fig. 3 Raman spectroscopy of MWCNTs a) Pristine MWCNTs b) five hour ball-milled MWCNTs c) ten-hour ball-milled MWCNTs d) ten-hour ball-milled MWCNTs

Table 1 Raman Spectra of pristine and processed materials

Multi-wall carbon nanotubes	D band Intensity, ID	G band intensity, IG	G’ bandIntensity, IG’	The ratio of ID and IG
Pristine	1363	1843	1073	0.738
Five hour ball-milled	1245	1745	1024	0.713
Ten hour ball-milled	1266	1765	977	0.717
Twenty hour ball-milled	1276	1268	757	1.01

Surface modification of Multi-wall carbon nanotubes

Due to their long length, MWCNTs incline to form agglomerate and large clusters when dispersed in an oil medium. Further, during the process of ball-milling, the MWCNTs are compacted by the balls creating large groups of tangled MWCNTs. To separate the groups and make the CNTs remain stable in the oil, it is essential to alter the surface of MWCNTs with a surfactant to generate steric repulsions between individual nanotubes. A surfactant SPAN 80 (Sorbitaanmonooleate), a nonionic surfactant with the hydrophilic-lipophilic balance of about five is used to stabilize the nanoparticles in the oil medium by modifying the surface of MWCNTs. SPAN 80 adsorbs on the outer surface of MWCNTs decreasing their surface energy averting agglomeration and settlement of nanoparticles. To make surface assisted MWCNTs SPAN 80 and MWCNTs are mixed in a solvent in the ratio of 2:1and processed in an ultra-sonicator for 30 min to create a mechanochemical reaction. The reaction covers the surface of the MWCNTs with surfactant creating steric repulsions between individual tubes.

FTIR spectroscopy

To characterize the surface modification process for functional groups on the outer surface, the surface assisted MWCNTs are tested on a Fourier transforms infrared spectroscope. Fig. 4a shows pristine MWCNTs indicating no characteristic peak. FTIR images of surface-modified MWCNTs is shown in Fig. 4b with characteristics peaks in the wavelength range of 1465 and 1488 cm^{-1}signifying lipophilic groups latched on to the surface.

Preparation of lubricants with Multi-wall carbon nanotubes and evaluation of stability

The long and ball-milled MWCNTs after surface modification are dispersed in lubricating oil in 0.25, 0.5 and 1wt % using a probe ultra sonicator. The stability of the oil samples is observed for sixty days through light scattering techniques using a zeta- sizer (Horiba SZ 100). Dispersion of ball-milled MWCNTs in gear oils could result in a more excellent stable suspension compared to long MWCNTs and could enhance tribological properties.

The zeta potential is a pointer for dispersion stability of MWCNTs in the lubricating oil, and a zeta potential value of ± 40 specifies excellent stability. The samples are analyzed for a period of 2 months for variation in zeta potential. Since the gear oil has a high viscosity and could not be processed in zeta sizer, the oil samples are diluted with toluene to increase their transmittance to record accurate values. Oil samples dispersed with ball-milled MWCNTs exhibit higher values of zeta potential. Fig. 5 show the difference in the value of zeta potential for samples immediately after preparation and 2 months after preparation.

Fig. 5a and 5b show the differences in the zeta potential of oil dispersed with long MWCNTs after preparation and 2 months after preparation, respectively. It can be observed that long MWCNTs exhibit lower stability characterized by low zeta potential. Fig. 5c&5d show the changes in the zeta potential of oil dispersed with ten-hours ball-milled MWCNTs, and it can be seen that oil with ten-hours ball-milled MWCNTs possesses higher dispersion stability. The effect of weight fraction on zeta potential is also investigated, and Table 2 gives a variation of zeta potential during 60 days for different test samples. As can be seen from the table there is a strong influence of size (ball-milling duration) and weight fraction of MWCNTs on the zeta potential and hence the stability of the fluids. Weight fraction above 0.5 % gave poor dispersion of oil.

Further, as the length of MWCNTs, the chance of agglomeration is less and hence excellent dispersions are achieved characterized by high zeta potentials. Among all oils with twenty hours MWCNTs displaying highest stability. A lower agglomeration rate due to shortening of MWCNTs is the reason for more excellent stability. However, the defect formed in twenty-hours ball-milled MWCNTs makes them vulnerable at higher loads in tribological testing.

Table 2 Zeta potential of test oil dispersed with Multi-wall carbon nanotubes

Sample	Zeta potential (mV)	
	1st day	After 2 months
Base oil + 0.25 wt% long Multi-wall carbon nanotubes	-21.9	-20.8
Base oil + 0.5 wt% long Multi-wall carbon nanotubes	-16.4	-14.2
Base oil + 1 wt% long Multi-wall carbon nanotubes	9.4	-10.2
Base oil + 0.25 wt% five-hour Ball-milled Multi-wall carbon nanotubes	53.2	-31.9
Base oil + 0.5 wt% five-hour Ball-milled Multi-wall carbon nanotubes	-41.6	20.8
Base oil + 1 wt% five-hour Ball-milled Multi-wall carbon nanotubes	10.8	6.6
Base oil + 0.25 wt% ten-hour Ball-milled Multi-wall carbon nanotubes	-60.5	-44.2
Base oil + 0.5 wt% ten-hour Ball-milled Multi-wall carbon nanotubes	-50.2	-40.4
Base oil + 1 wt% ten-hour Ball-milled Multi-wall carbon nanotubes	-25.4	22.8
Base oil + 0.5 wt% twenty-hour Ball-milled Multi-wall carbon nanotubes	-72.9	-70.6
Base oil + 1 wt% twenty-hour Ball-milled Multi-wall carbon nanotubes	-50.4	-48.2

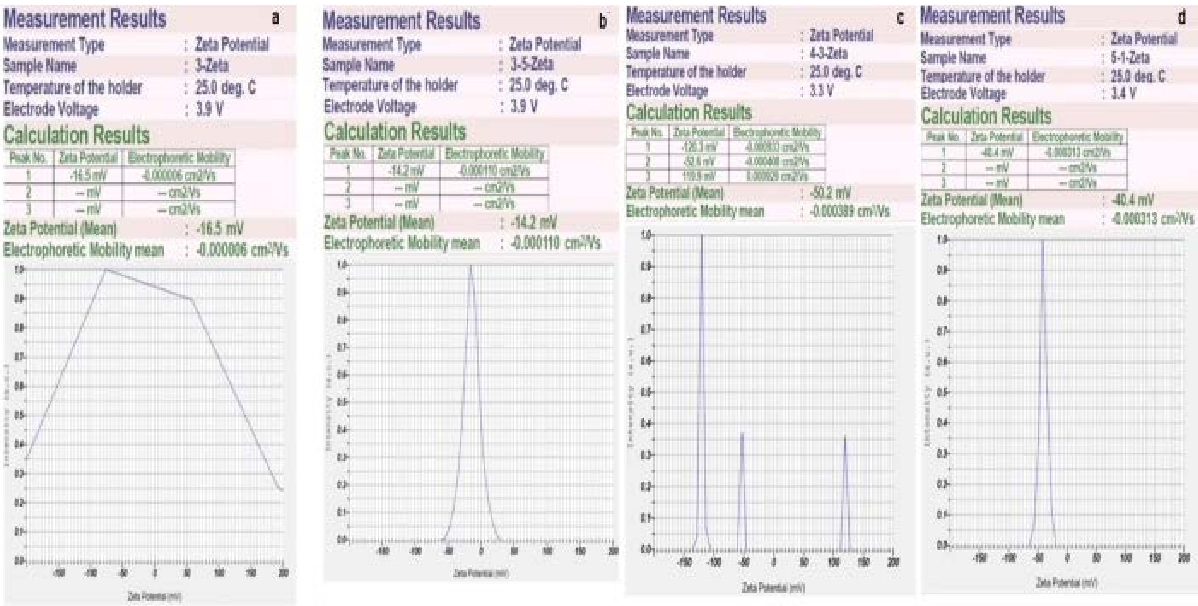

Fig 5. Zeta potential variation of nanofluids during 60 days A)Lubricants with long MWCNTs immediately after preparation B)lubricant with long MWCNTs after 60 days C) lubricant with ten hours Ball-milled MWCNTs shortly after preparation D) lubricant with ten-hour Ball-milled MWCNTs after 60 days

Tests for tribological properties

Four -ball tester is used to test the nanofluids for their tribological properties. In the experiments, three balls were fixed stationary in the lower chamber called a ball pot and filled with the test sample and are forced against a rotating top ball (fourth Ball).

Three separate tests for anti-wear, anti-friction, and extreme-pressure properties are conducted as per ASTM standard. The test parameters of load, duration, temperature and speed of rotation are taken as per standard test procedures. The details of test conditions are as shown in Table. 3.

In wear test, the capability of the oil to inhibit wear is judged by the average scar diameter appearing on the lower three balls. A smaller scar diameter indicates good anti-wear behaviour. In friction test, “wear in” is initially conducted for one hour at a speed of 600 RPM and at a load of 40 kgf, with maintaining oil at 75°C temperature. After the process of wear in, the lubricating oil used in the test is removed, and balls are cleaned without changing the position of the balls.

Table.3 Test conditions during anti-wear, anti-friction and extreme pressure tests

Test method	Test	Conditions during test
ASTM D 4172	Wear test	Duration : 1 hour; Load: 40 kgf, Speed: 1200 RPM; Temperature of oil: 75°C
ASTM D 5183	Friction test	**Wear in** Duration : 1 hour; Load: 40 kgf, Speed: 600 RPM; The temperature of oil: 75°C **Friction test** Speed: 600 RPM; Temperature of oil: 75°C Loading starts from ten kgf increased in succession of ten kgf every ten minutes till seizure characterized by a sharp increase in the coefficient of friction occurs.
ASTM D 2783	Extreme pressure properties	ten successive tests at room temperature with fresh lubricant and new balls in each test Duration: ten seconds; Load: 80 kgf till welding of balls occurs, Speed: 1760 RPM; Temperature of oil: 5°C

The ball pot is filled with fresh oil sample and with the same worn balls; the test is restarted as per second friction test protocol with a starting load of 10 kgf, and after each successive ten min interval, weight – fraction load is continuously increased by 10 kgf until sharp increase in the frictional torque is observed which specifies incipient seizure which is one of the crucial factors in assessing the efficacy of the oil.

The properties under extreme-pressure conditions prevailing on the oil due to high loads are determined by ASTM D 2783 in terms of the load-carrying capacity and weld load. The test sequence follows a series of ten tests of ten-second conducted on the oil till the point the oil vaporizes under high temperature and pressures and the top and bottom three balls gets welded. The ability of lubricating oil in resisting weld conditions is called the load wear index(LWI), and it is calculated as per the relation is given below.

LWI = (A/10), (kgf). Where A = total of all the corrected loads calculated during the series of ten tests preceding the weld load and $\text{Corrected load} = \frac{LD_H}{X}$ (1).

Where L = load applied during test, kgf, X = average wear - scar diameter on all the bottom 3worn balls in mm and $\text{Hertz scar diameter}, D_H = 8.73 \times 10^{-2}(L)^{1/3}$ in mm.

RESULTS AND DISCUSSION

The Figs. 6a, 6b &6cshow the test results of wear and friction tests. From the Figures, it can be observed that the mean wear – scar and coefficient of friction of oil with MWCNTs are much lesser than that of base oil.

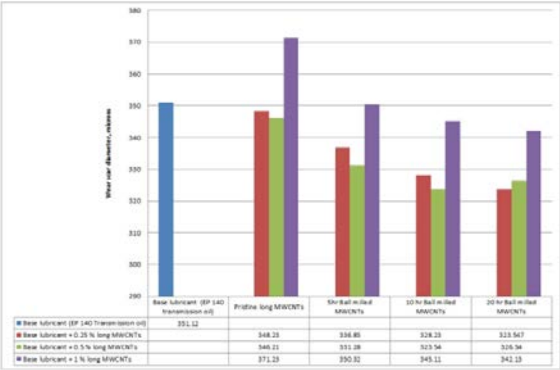

Fig. 6a Variation of wear - scar diameter of test samples

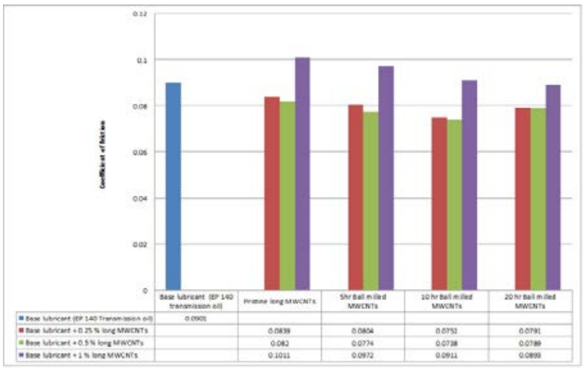

Fig. 6b Variation of friction coefficient of test samples

The seizure load of the oil is also found to have improved with the dispersion of ball-milled MWCNTs. Moreover, the weight per cent is also found to have a profound influence on the wear and friction properties. Oils with 0.25 wt% could improve the anti-wear performance, but oils outperform it with 0.5 wt%. The oil with 1 MWCNTs performed poorly in all tests. Ball-milled MWCNTs due to their more excellent stability owing to shorter length performed consistently, and oil dispersed ten-hours ball-milled MWCNTs gave the best output.

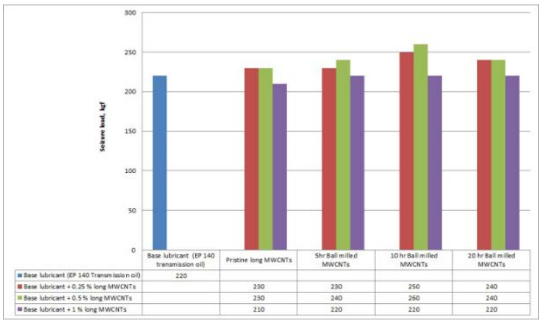

Fig. 6c Variation of seizure load of test samples

The variation of the friction torque concerning the time is shown in Fig. 7. It can be seen from the graph the effect of ball-milling, as well as the weight per cent of nanomaterials, has improved the properties at higher loads. The surfaces are separated with a thin film of oil during boundary lubrication regime, Any raise in the load would slide the oil out of the contact area.

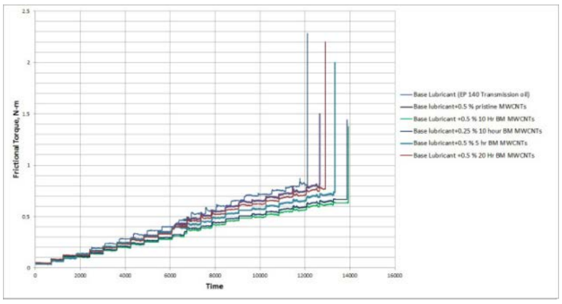

Fig. 7. Variation of friction torque with the time during friction test

Decreasing the thickness of oil film, thereby the chance of contact between surfaces is high during running conditions. However, in case of the oil dispersed with shortened MWCNTs the shortened MWCNTs, they could smoothly glide and roll like spacers between the two contacting surfaces increasing the pressure limits of the oil thus drastically decreasing the coefficient of friction and increasing the seizure load. Thus, the oils dispersed with ball-milled MWCNTs have exhibited steady performance on the torque - time plot compared to the base oil. In friction test also the oil with 0.25 % and 0.5 % ten-hour ball-milled MWCNTs performed very well.

From both friction and wear tests, it can also be observed that the effect of weight - fraction and ball milling are predominant in improving the tribological properties of gear oil. Overall oil with ten-hours ball-milled MWCNTs dispersed in 0.25 Wt % and 0.5 Wt% gave the best results. The extreme-pressure features last non-seizure load, weld load (WL) and load ball-mill wear index of test oils under consideration are summarized in Table 4. An enhancement in the last non-seizure load, weld load (WL) and load wear index was observed dispersion of MWCNTs. A graph showing the variation of wear - scar diameter with pressure is shown in Fig. 8. The regions as shown in Fig. 8 are generally designated as anti-wear region, seizure load region and extreme-pressure region.

Table 4 extreme pressure test results

Test oil	Last non-seizure load, kgf	weld load, kgf	load wear index
Base oil (EP 140 transmission oil)	120	250	65.23
Base oil + 0.5 % long Multi-wall carbon nanotubes	120	315	68.84
Base oil +0.5 wt% five-hour Ball-milled Multi-wall carbon nanotubes	140	315	70.11
Base oil +0.25 wt% ten-hour Ball-milled Multi-wall carbon nanotubes	140	315	74.32
Base oil + 0.5 wt% ten- hour Ball-milled Multi-wall carbon nanotubes	140	400	76.98
Base oil + 0.5 wt% twenty -hour Ball-milled Multi-wall carbon nanotubes	120	250	71.32

In the anti-wear region, all the oilsshowed similar behavior. The area above last non-seizure load characterized by a sharp rise in the wear – scar is called extreme-pressure zone in which high pressures and temperatures are encountered by gear oil, and the additives of a gear oil are required to endure these extremes. MWCNTs could form a barrier between the surfaces resisting the extreme conditions to increase weld load (WL) due to their excellent mechanical properties.

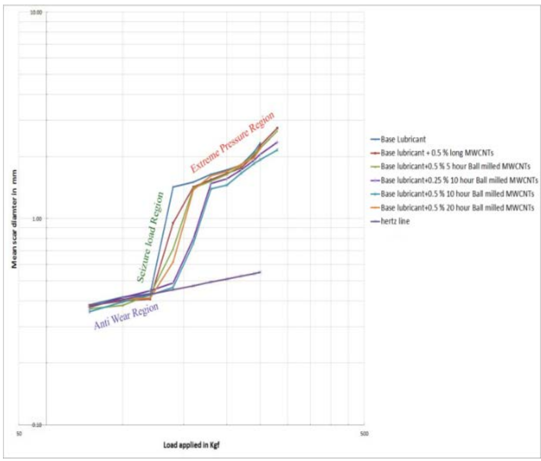

Fig. 8 variation of wear - scar diameter with the applied load during EP test

There is a decrease in the wear - scar diameter of lubricant with pristine and ball-milled MWCNTs and the effect of dispersion of shortened MWCNTs is seems to be quite noticeable in this region. Oil dispersed with 0.25 and0.5 Wt%tenhourball-milled Multi-wall Carbon nanotubes owing to improved dispersion due to short length, enhanced the seizure load and could diminish the wear - scars even in the extreme-pressure regions. Gear oil with twenty hours ball-milled MWCNTs improved the load wear index by performing well in the anti-wear area but failed in EP region creation of defect during ball milling.

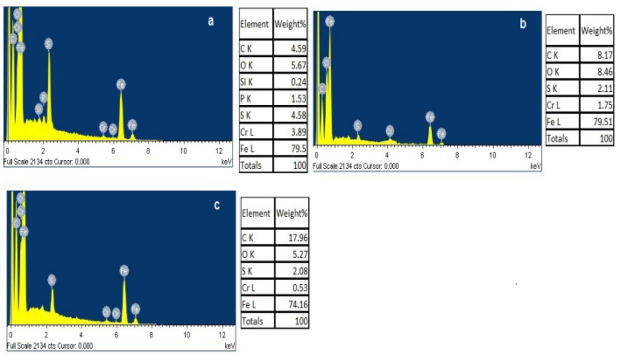

Fig. 9 EDX spectrum of the worn ball a) tested with base lubricant b) examined with lubricant dispersed with 0.25 % ten-hour BM MWCNTs c) tested with lubricant dispersed with 0.5 wt% ten-hour BM MWCNTs

In the anti-wear region, dispersion of ball-milled MWCNTs in oil decreased the coefficient of friction, thereby giving lower wear - scars on the test balls. This is evident from the fact that after last non-seizure load, the wear - scar diameter with the dispersion of MWCNTs is considerably low, resulting in improved load wear index as well as weld load. Furthermore, it can also be seen from Fig. 8 that oil with 0.25 % and 0.5 % weight fraction often-hour ball-milled MWCNTs gave the best performance.

ANALYSIS OF THE WORN SURFACES AFTER THE EP TEST

To assess the likely reason for the enhancement of extreme-pressure properties with the dispersion of

MWCNTs in the oils, metallographic studies were conducted. The worn surfaces of balls before weld load (WL) are analyzed with EDX. From the analysis, it is found that the MWCNTs under extreme-pressure conditions deposit on the surfaces in contact, which result in attrition of MWCNTs leading to deposition of the carbon layer. This carbon layer on the surface resulted in reduced friction, thereby improving the wear properties. The enhancement of wear properties resulted in increased seizure load resulting in increased weld load (WL) and improved extreme-pressure properties. The formation of the carbon layer is found to be higher for ball-milled MWCNTs since pristine MWCNTs forms hard clusters which are much harder that of individual ball-milled MWCNTs. This result in more deposition of carbon on the surface with oil dispersed with ball-milled MWCNTs compared to pristine MWCNTs and hence greater property enhancement. Fig. 9shows the EDX analysis of wear - scar area on the balls during EP tests. From the figure, it can be seen that for base oil protection under wear and extreme-pressure conditions were done by Sulphur and Phosphorous additive deposition on the scar surface. With oils dispersed with 0.25 % and 0.5 % MWCNTs along with Sulphur, carbon also deposited on to the surface giving additional protection thus decreasing the friction and improving wear and extreme-pressure (EP) properties. The deposition with 0.5 % Multi-wall carbon nanotubes is more than 0.25 % Multi-wall carbon nanotubes which resulted in the more excellent performance of the former.

CONCLUSIONS

1. The shortening of multi-walled carbon tubes by ball-milling of before dispersion in the oil is found to be crucial in enhancing the dispersion stability, anti-friction, anti-wear and extreme-pressure properties of the lubricating oil.
2. The defect formation on the Multi-wall carbon nanotubes after ball-milling was observed from Raman spectroscopy and it was found that although the ball-milling time of up to ten hours did not yield any defects on the surface of Multi-wall carbon nanotubes mild defects were observed when the ball-milling time is twenty hours.
3. Shortened Multi-wall carbon nanotubes could remain stable in the oil for more than two months.
4. Despite the surface modification, long Multi-wall carbon nanotubes when dispersed in oils exhibited poor stability and could slightly improve the anti-friction and extreme-pressure properties.
5. Dispersion of shortened Multi-wall carbon nanotubes in gear oils could substantially improve the wear - scar diameters and friction coefficients. During contact between friction surfaces, short length Multi-wall carbon nanotubes could slide between mating surfaces decreases friction.
6. The load wear index (LWI) and weld load (WI) of oils dispersed with shortened Multi-wall carbon nanotubes have improved significantly as the performance of short Multi-wall carbon nanotubes are far higher in both anti-wear and extreme-pressure region.
7. Too short Multi-wall carbon nanotubes despite forming good suspension could not give the best performance due to the formation of defects. Thus an optimum length of about 6 microns of Multi-wall carbon nanotubes dispersed in oil could give the best results.
8. Deposition of the carbon layer on the rubbing surface is found to be the reason for the greater performance of oils dispersed with Multi-wall carbon nanotubes.
9. Ball-milling is also found to have necessitated lesser weight -fraction of Multi-wall carbon nanotubes for improving the tribological properties.

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