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Nanocomposite UHMWPE–CNT Polymer Coatings for Boundary Lubrication on Aluminium Substrates

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Abstract

The boundary lubrication regime plays a very important role in determining the life span of any of the two mating parts under liquid-lubricated conditions. It is during the start\stop cycles when insufficient fluid is available to fully separate the surfaces in relative motion and thus unusual wear takes place; a case of boundary lubrication. The aim of this work is to study the feasibility of using polymer coatings as boundary lubricants. This study investigates the friction and wear properties of ultrahigh molecular weight polyethylene (UHMWPE) films coated on aluminium substrates under dry and base oil (without any additives)-lubricated conditions. In order to increase the load bearing capacity of the UHMWPE coatings, 0.1 wt% of single-walled carbon nanotubes are added. Experiments are carried out on a custom-built tribometer simulating a line contact between a polymercoated cylindrical Al surface (shaft) and a flat uncoated Al plate as the counterface. The experimental parameters such as the normal load and the sliding speed are selected to simulate the boundary and mixed lubrication regimes for comparison purposes. Specific wear rates of the polymer films and bare Al surface under lubricated conditions are also calculated. Stribeck curves have been generated to evaluate the effectiveness of the pristine UHMWPE and the nanocomposite coatings in the various regimes of lubrication, especially the boundary lubrication regime. It is observed that the selected polymer coatings are effective in protecting the metallic surfaces without causing any observable oil contamination with wear debris.

Keywords Ultra-high molecular weight polyethylene (UHMWPE), Single-walled carbon nanotubes (SWCNTs), Boundary lubrication, Polymer films

The current state of lubrication for many contacting surfaces in mechanical systems is the use of protective coatings on surfaces and the use of lubricants with the appropriate additives [1]. Important properties of a coating for machine element applications are, beside good adhesion to the substrate, a combination of high wear resistance and low coefficient of friction. Also the wear of the uncoated counter surface is critical. Various protective coatings that are in practice in the industry are different metal carbides (WC, TiC, CrC), diamond-like carbon, molybdenum disulphide (MoS2) and several physical vapour deposition coatings such as TiAlN, CrAlN, ZrN, ZrC, WC/C, W–C:H, TiO2, Al2O3, etc. [2–6]. Even though the use of these coatings provides high wear resistance, they suffer from disadvantages such as poor adhesion with the substrates [7], high friction, high thermal stresses in the coating, sensitive to the environment, incompatibility with the lubricant, etc. [8]. Any debris particle from such hard coatings can also be very damaging for the whole tribological system.

In view of the above challenges encountered in using the various protective coatings, much attention has been paid recently towards the development of additives through the understanding of their lubrication mechanism [8]. To enhance the performance of the lubricant, various additives are added to it. Commonly used additives in the lubricants are zinc dialkyl dithiophosphate and molybdenum dialkyl dithiocarbamate, etc. The function of additives is to react with contacting surface and form tribofilms which protect the surfaces from wear [9] especially during boundary lubrication. However, environmental and health issues constraint the extensive usage of these additives. Even though novel lubricant additives with improved performance for current lubricants [10, 11] are being researched, there is an equally important need to modify the lubrication strategies where the use of potentially harmful lubricant additives is reduced or fully eliminated.

2 Polymer Coatings in Sliding Components

Polymer coatings with their ability to be coated using simple techniques and their cost effectiveness present a very viable alternative protecting technology [12]. They are one of the most promising methods to enhance the wear life of various substrates since some polymers have exceptionally high wear resistance coupled with low friction, low density, good toughness, low cost and ease of fabrication into different shapes [13]. Polymer thin coatings have shown excellent tribological properties when deposited onto various metallic substrates such as steel and aluminium [14–18]. In spite of their very good tribological properties, polymer coatings have not been used to their full potential in the sliding mechanical components. If these polymer coatings are effectively used, it is possible to reduce the overall consumption of lubricants and at the same time reduce wear of the metal components with better overall life of tribological systems. Excellent wear resistance of the films will also allow the use of lubricants with low harmful additive contents or of bio-lubricants (such as soybean oil), leading to an environmental-friendly lubrication technology. In the presence of a thin layer of highly wear resistant polymer, there may not be any need of a boundary layer forming lubricant additive.

3 UHMWPE as a Polymer Coating

Ultra-high molecular weight polyethylene (UHMWPE) is a linear homopolymer with a simple composition of only hydrogen and carbon and it is produced by the polymerization of ethylene (C2H4) gas. The chemical formula for polyethylene is (C2H4)n, where n is the degree of polymerization. For UHMWPE, a single molecular chain can consist of as many as 200,000 ethylene repeat units and the molecular weight number is more than 2 millions [19]. UHMWPE is a unique polymer which has exceptional tribological properties. It has the highest sliding abrasion resistance and highest notch impact strength of any commercial plastic. Combined with abrasion resistance and toughness, the inherent low coefficient of friction of UHMWPE yields a self-lubricating non-stick surface. In its bulk form, UHMWPE is highly wear resistant compared to many other polymers such as polyetheretherketone, polyethylene (PE), polystyrene, etc. [19, 20]. The outstanding characteristics of UHMWPE can be maintained from -269 _C to 90 _C and even higher for shorter periods of time. Since it does not melt flow or liquefy at its softening point of 138–142 _C, it retains excellent dimensional stability at temperatures up to 200 _C [19]. Research on the tribological properties of UHMWPE films on bare Si surface and suitably modified Si surface has shown that UHMWPE is an excellent candidate material as thin coatings because of its very high wear resistance coupled with low coefficient of friction against metals and ceramic materials [21, 22]. UHMWPE was also coated successfully onto steel and Al substrates to improve the wear life of this metal [14, 18] by using the dip-coating process. The coating demonstrated a very good wear life with a low value of the coefficient of friction in the range of 0.02–0.2. Due to its high resistance to corrosive chemicals it can be used in conjunction with various lubricants as well. Moreover, nanocomposites of UHMWPE prepared by reinforcing the polymer with carbon nanotubes showed a significant improvement in its mechanical and tribological properties such as hardness, wear resistance and scratch resistance with only a small increase in the coefficient of friction [23]. Therefore, in this research we have chosen UHMWPE, in pristine form and as composite with CNT, as the protective polymer film material because of its low coefficient of friction, high wear resistance, moderate thermal stability, good corrosion resistance and the ease of deposition using the simple dip-coating method.

3.1 Carbon Nanotubes as Effective Filler Materials

In spite of its excellent properties, use of UHMWPE in demanding tribological applications has been limited due to various constraints such as its low load-bearing capacity and thermal instability. Addition of reinforcements-like carbon nanotubes is one approach to overcome these constraints. Carbon nanotubes (CNTs) due to their excellent mechanical (exceptionally high tensile strength and stiffness), electrical and thermal properties (thermal conductivity of 3000 W/mK) have caught the attention of researchers in the recent years and are being considered as a potential filler material for many polymer matrices. Several studies have shown that the addition of CNTs resulted in significant improvements in the mechanical properties such as the elastic modulus and strength of the polymer matrices [24–26]. An increase in the wear resistance of bulk UHMWPE with the CNTs addition has also been observed [27–30]. Recently, Abdul

Samad and Sinha [23] have effectively reinforced the UHMWPE coatings with CNTs and observed a remarkable improvement in the mechanical, tribological and the thermal properties of the nanocomposite film.
Aluminium (Al) is selected as the substrate material because of its extensive use in the automobile/aerospace industries. Its high strength-to-weight ratio combined with its abundance makes it a widely used material in various tribological applications as well. Moreover Al, being corrosion resistant due to its adherent aluminium oxide layer (Al2O3), is useful for applications requiring a longer life. However, Al is a soft and ductile material with very poor tribological properties. Dry sliding of Al with metals, such as steel or itself, yields high coefficient of friction ([0.6) and very short wear life if at all. Polymer coatings have been used to improve the tribological properties of Al which showed a remarkable improvement in its wear life [18].

Thus, the main focus of this article is to investigate the feasibility of developing a lubrication strategy using the nanocomposite UHMWPE polymer coating reinforced with CNTs on aluminium substrates, in combination with an oil lubricant (base oil without any additives).

4 Experimental Procedures

4.1 Materials and Chemicals

Aluminium cylindrical shaft of 40 mm diameter and a flat Al plate of (15 mm 9 15 mm) were used. In the context of a simple journal bearing application, the cylindrical shaft acts as a journal while the flat plate acts as the bearing housing to simulate a continuous line sliding contact. The cylindrical shaft was coated with the polymer and the nanocomposite films and the bare flat Al pin was used as the counterface. Figure 1a shows the experimental setup used to conduct the wear tests. Figure 1b shows the geometry of the aluminium flat pin (Ra = 0.4 ± 0.05 lm) and cylindrical shaft on which the polymer film was deposited. The oil reservoir used is shown in Fig. 1c and the schematic of the line contact is shown in Fig. 1d.

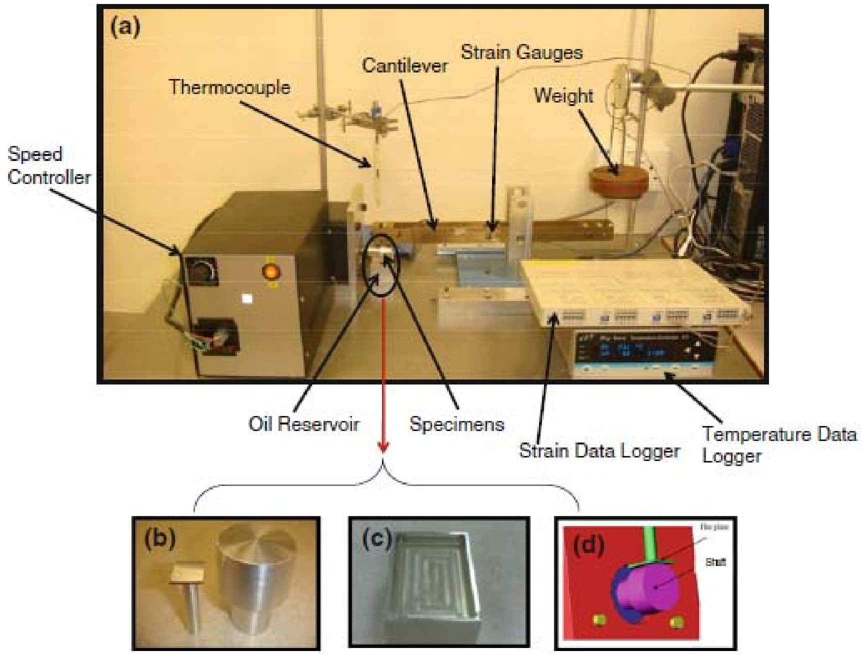

Fig. 1 **a** Different components of the experimental setup. **b** The geometry of the samples used in the wear tests. **c** The oil reservoir used to hold the lubricant. **d** A schematic of the line contact simulation during the wear tests

UHMWPE polymer powder (Grade: GUR X 143) used for coating the specimens was supplied by Ticona Engineering Polymers, Germany, and was procured from a local Singapore supplier (Melt index MFR 190/15 = 1.8 ± 0.5 G/10 min; bulk density = 0.33 ± 0.03 g/cm3; average particle size = 20 ± 5 lm). Decahydronapthalin (decalin) was used as a solvent to dissolve the polymer powder prior to dip-coating. Single-walled carbon nanotubes (SWCNTs) (diameter = approx. 10 nm) were procured from Iljin Nanotech Co. Ltd., South Korea, which were as-processed grade and were produced using the arc-discharge process. SN 150 Base oil (Group I), which has no additives and an industrial bearing lubricant Beslux Atox 32, was used as the lubricants in the experiments with viscosity indices of 100 and 105, respectively. They were supplied by Premier Six Pte Ltd. and Tecsia Lubricants Pte Ltd., Singapore. The properties of the base oil (SN 150) and the industrial oil are shown in Table 1.

Table 1 Properties of the SN 150 base oil and the industrial oil

Property	SN 150 base oil (Group I)	BESLUX ATOX-32
Kinematics viscosity at 40 °C (cSt)	28–34	28.8–35.2
Kinematics viscosity at 100 °C (cSt)	5.2–5.4	–
Viscosity index	100	105
Flash point (open cup) (°C/min)	200	170
Density (kg/m^3)	868	–

4.2 Preparation of the Film on Al Substrates

4.2.1 Pristine UHMWPE Film

To prepare the UHMWPE polymer solution, decalin was used as a solvent. Our earlier studies have shown that 3 wt% of UHMWPE powder in decalin solution results in a film with optimum tribological properties [14]. Based on our past studies, 3 wt% of UHMWPE powder is mixed with the decalin solution and heated to a temperature of 170 ^{O}C for 1 h to allow the complete dissolution of the powder. Magnetic stirrers were used for uniform distribution of heat in the solution and for speeding up the dissolution process. The Al samples are plasma-treated (RF power of 30 W for 5 min) prior to coating to clean the surface of any contaminants and increase the surface-free energy to improve the adhesion between the film and the substrate [14]. Coating deposition was carried out immediately after the plasma treatment using a custom-built dipcoating machine at a constant dipping and withdrawal speeds of 2.1 mm/s. The samples were held in the solution for 30 s and then withdrawn at the same speed to obtain a uniform film thickness of 55 ± 4 lm. To ensure the complete evaporation of the solvent, the Al samples were subjected to a step-wise heat treatment in a hot plate oven for 20 h at a temperature of 120 ^{O}C, before being stored in desiccators for further mechanical and tribological testing.

4.2.2 Nanocomposite UHMWPE Film

The SWCNTs were functionalized by plasma treatment using the Harrick Plasma (USA) equipment, prior to mixing them with the polymer matrix. Recently plasma treatment which is an environmental-friendly and a less time consuming process has been used effectively to functionalize the SWCNTs to achieve strong bonding between the nanotubes and the polymer matrix and also to obtain a uniform dispersion of the SWCNTs [31–34]. SWCNTs were spread out uniformly in a flat crucible and placed inside the plasma chamber to ensure that most of the SWCNTs were exposed to the plasma. Before the plasma treatment the base pressure inside the plasma chamber was lowered to approx. 30 mTorr. Once the SWCNTs were plasma-treated, appropriate amount of decalin was added to the SWCNTs and ultrasonicated using the Sonics VCX-130 (Sonica & Materials Inc., USA) ultrasound homogenizer for 12 min with a 30% amplitude and a cycle on/off time of 20/5 s to ensure uniform dispersion without major agglomeration. Studies have shown that effective change in lengths of nanotubes through sonication occurs within 12 min and minimal shortening happens beyond this time duration [35]. After the sonication, 3 wt% of UHMWPE powder was added to the solution and subjected to mechanical stirring for 20 min for proper mixing of the SWCNTs and the polymer powder. The mixture was then heated at 170 _C for about an hour to ensure the complete dissolution of UHMWPE. Magnetic stirrers were used for uniform distribution of heat in the solution and for speeding up the dissolution process. The solution was prepared using 0.1 wt% of SWCNTs. The dip-coating procedure adopted here is similar to what has been presented earlier for the pristine UHMWPE film.

4.3 Surface Characterization and Analysis

Surface roughness and the profile of the wear track of the pristine polymer and the nanocomposite coatings were measured using the Wyko NT1100 Optical profiler (Veeco, USA). The scan area used was 300 µm X 230 µm. The surface morphology of the coatings and the wear tracks were studied using field emission scanning microscopy (FESEM). Prior to FESEM imaging, the samples were gold coated at 10 mA for 40 s using a JEOL, JFC- 1200 Fine Coater.

4.4 Nanoindentation Tests

Nanoindentation tests were performed using an MTS Nano Indenter XP machine on the nanocomposite polymer films to evaluate the effect of the lubricating base oil on its hardness and elastic modulus. The samples were indented using a constant load of 500 µN with a standard Berkovich diamond tip. A total of eight repeats of indentation were carried out and the reported value is the average of the eight data. The loading and the unloading rates were kept constant at 50 µN/s, with a holding time of 10 s at the final depth of indentation.

4.5 Tribological Characterization

A custom-built plate-on-cylinder tribometer was used to simulate the line contact. Figure 1a shows the experimental setup used to conduct the wear tests. The principle of operation of this tribometer is a shaft mounted onto an AC motor where a speed controller drives the cylindrical shaft at variable speeds. The loading weights are used to transmit a normal force onto the flat plate pivoted at one end of the cantilever arm. The strain gauges attached to the cantilever beam measure the frictional force which is determined by the cantilever beam deflection during loading. The output voltage is transmitted to a digital data logger from KYOWA BRAND PCD-300A. The transmitted data (frictional force) are displayed graphically as a function of frequency onto a computer with the aid of software (PCD Reader). Furthermore, a thermocouple ‘‘type t’’ was used to measure the temperature change of the oil in the oil reservoir. The tribometer is used to measure the coefficient of friction, wear life and wear rate of the pristine and the nanocomposite UHMWPE coatings under dry and lubricated conditions. In this study, the cylindrical shaft was coated with a thin film instead of the flat plate because this study aims to simulate a more realistic experiment where the shaft acting as a journal is coated and undergoes wear at various conditions in terms of load and speed, hence providing a more realistic wear life and wear rate. An oil reservoir was designed to provide the rotating shaft with continuous supply of the lubricant to conduct the tests under simulated lubricated conditions. In addition, a thermocouple was introduced during lubricated conditions to observe how temperature of the lubricant contained in the oil reservoir changed with time during the experiments. The experimental parameters such as the loads and rotational speeds are selected to simulate the boundary and mixed lubrication regimes for evaluating the effectiveness of the nanocomposite coating in protecting the Al surface (the substrate and also the counterface).

5 Results and Discussions

5.1 Evaluation of the Pristine and Nanocomposite Coating Under Dry Conditions

Wear tests were conducted at a normal load of 45 N and rotational speed of 272 rpm (linear speed = 0.57 m/s) under dry conditions to evaluate the tribological performance of the pristine and the nanocomposite polymer films. In this study, the criteria for the film failure under dry conditions is taken as when the coefficient of friction exceeds a value of 0.3 or when continuously large fluctuations are seen in the coefficient of friction curve, whichever happens first [36]. Figure 2 shows the comparison of the wear lives and the coefficients of friction for the two coatings. It is observed that the pristine UHMWPE film shows a wear life of 250,000 cycles when compared to that of the nanocomposite film which did not fail until approximately 2 million cycles (experiment was stopped due to the long test duration). This considerable increase in the wear life of the film is attributed to the excellent mechanical and thermal properties of CNTs [23]. There is a slight increase in the coefficient of friction for the nanocomposite coating which can be because of the increase in the shear strength of the nanocomposite film [27]. The CNT presence renders the film strong and the top layer is not able to plastically shear in the same way as it would without CNT. This results in slightly greater resistance to sliding motion.

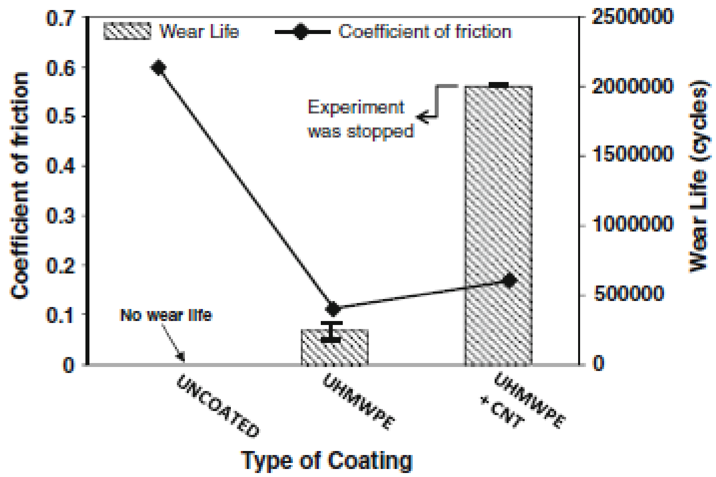

Fig. 2 Comparison of the coefficients of friction and wear life for the uncoated Al shaft, UHMWPE coated and UHMWPE + CNTs coated shafts against Al flat plate under dry sliding conditions

Figure 3a shows the cylindrical shaft coated with the nanocomposite coating after the wear test which was run until 2 million cycles. As can be seen from the figure that the length of the cylindrical part is about 20 mm and the length of the flat Al plate which is used as the counterface is about 15 mm. Thus after the test, both the wear track and the non-worn region can be seen on the cylindrical part which is also shown very clearly in the FESEM image in Fig. 3b. EDS analysis was conducted on the worn and the non-worn regions as shown in Fig. 3c, d. The presence of the strong carbon peak which corresponds to the polymer coating in the EDS spectrum confirms that the film has not failed even after 2 million cycles. As can be seen from the FESEM image in Fig. 3d, the polymer film has been smoothened-out without causing much wear to the nanocomposite coating. The RMS roughness values of the unworn and worn parts of the coating were measured as 2.42 and 1.86 µm, respectively. There was no wear observed even on the counterface Al flat plate with nearly no polymer transfer.

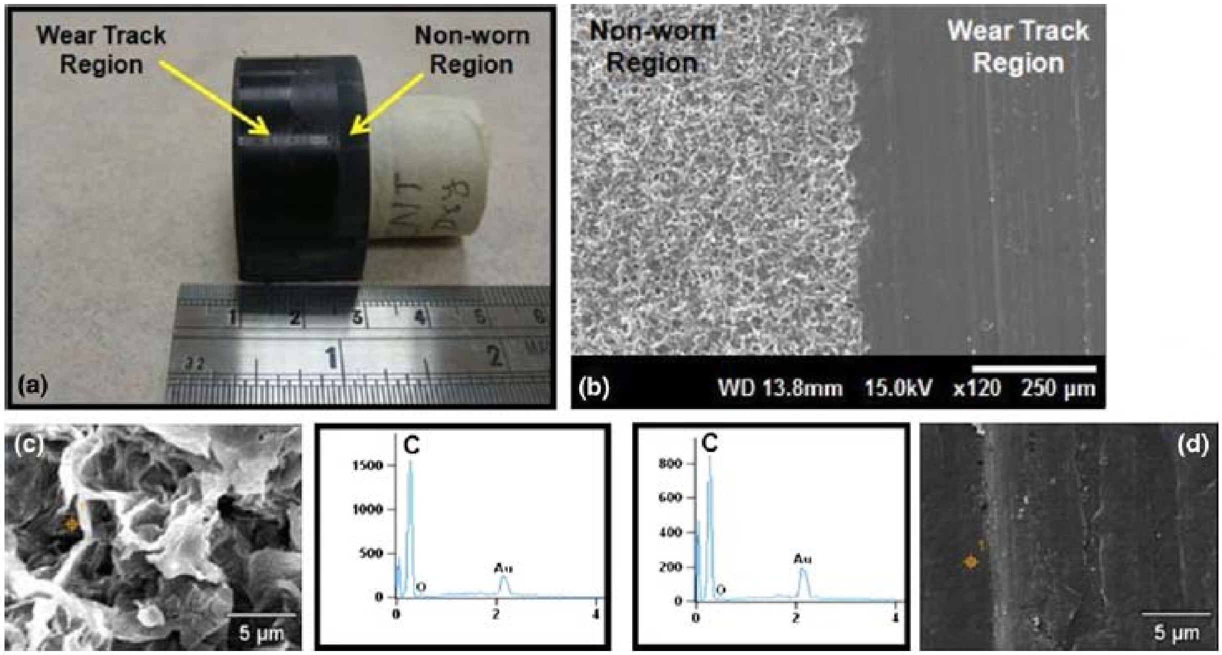

Fig. 3 a The nanocomposite (UHMWPE + CNTs) coated sample after 100 h of wear test under dry conditions under a load of 45 N and a linear speed of 0.57 m/s. b FESEM image of the wear track and the unworn region of the coating after 100 h of wear test under dry conditions with a load of 45 N and a linear speed of 0.57 m/s. c EDS spectrum for the unworn part of the nanocomposite coating. d EDS spectrum on the wear track after a test of 100 h under dry conditions with a load of 45 N and a linear speed of 0.57 m/s

5.2 Evaluation of the Pristine and Nanocomposite Coating Under Lubricated Conditions

Wear tests were conducted under lubricated conditions using a Group I base oil (without any additives) SN-150. Lubricated tests were conducted for the uncoated Al shaft on Al flat plate, UHMWPE coated and nanocomposite film (UHMWPE\CNTs) coated Al shafts on Al pins.

5.2.1 Stribeck Curves

Stribeck curve is a very important tool for identifying the boundary, mixed, elastohydrodynamic and hydrodynamic lubrication regimes in a lubricated contact. It gives a relationship between the coefficient of friction and the Sommerfeld number ($\eta V/P$), where g is the viscosity of the oil, V is the relative velocity and P is the apparent pressure at the point of contact. In this study, part of the Stribeck curve was generated for the lubricated sliding with base oil at a normal load of 45 N and varying speeds ranging from 0.062 to 0.833 m/s, respectively. The viscosity of the lubricating oil is assumed to be constant as the temperature of the oil remained constant at 25 ^{O}C through out the experiment. At each speed the experiment was run for approximately 20 min to let the reading for the coefficient of friction stabilize and then the average value is calculated. Figure 4 shows the Stribeck curves generated for the three conditions, namely, uncoated, UHMWPE coated and the nanocomposite film coated, respectively, under the base oil lubrication. It can be observed that for the uncoated Al sample, the lubrication regimes are very well defined from boundary to mixed lubrication regime. However, for the polymer coatings, there is not much change in the coefficient of friction with increasing speed, indicating the effectiveness of these films to protect the metal substrate from any wear and tear especially in the boundary to mixed lubrication regime. Nevertheless, there is a slight increase in the coefficient of friction from 0.09 to 0.1 in case of the nanocomposite film when compared to that of the pristine UHMWPE film. This can be because of the increase in the shear strength of the film due to the addition of the CNTs.

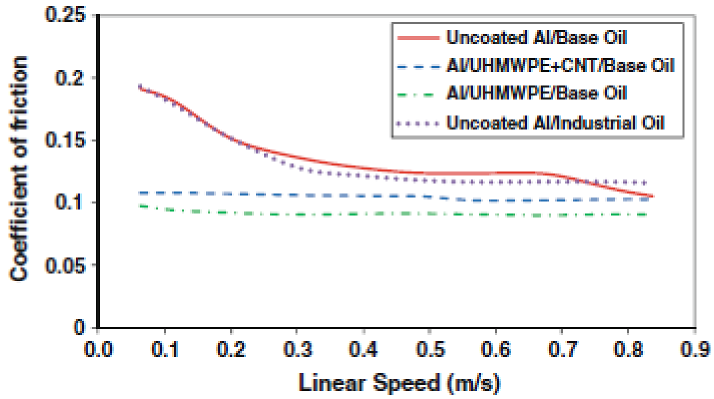

Fig. 4 Stribeck curves for the uncoated Al shaft, UHMWPE-coated and UHMWPE + CNTs-coated shaft against flat Al plate under base oil (SN 150) lubricating conditions under a constant load of 45 N. Data for uncoated Al shaft under industrial lubricant are also provided for comparison

5.2.2 Evaluation of the Nanocomposite Coating Under Boundary Lubrication

The main characteristics of the boundary lubrication regime are that there is a considerable interaction between the asperities of the two mating surfaces resulting in increased wear. In this regime, the friction and wear are determined by the surface properties as well as the properties of the lubricants and the applied load is shared between the asperity contacts and the lubricant pressure generated by the squeezed film between the surfaces. To evaluate the effectiveness of the nanocomposite film which showed exceptional tribological properties under the dry conditions in protecting the metal substrate, wear tests were also carried out under boundary lubrication conditions at a higher normal load of 60 N and a sliding speed of 0.11 m/s for 100 h test duration. As evident from the Stribeck curves (Fig. 4), these conditions correspond to the boundary lubrication regime. To ascertain the same, oil film thickness under the above conditions is measured and compared with the roughness values of the two counterfaces. The oil film thickness is measured by using the equation for the cylinder on flat plate (line contact) [37]:

$$h_0 = 2.08R(UG)^{8/11}W^{\frac{-1}{11}}$$

Where:

$U = \eta_0 \bar{u} / (E^* R)$ - a dimensionless speed parameter, $G = \alpha E^*$ - a dimensinless material parameter, $W = W_Z / (E^* R)$ - a dimensionless load parameter where W_Z is the normal load per unit width of the cylinder, E^* = effective modulus $\left[\frac{1}{E^*} = \left\{\left(\frac{1-\nu_1^2}{E_1}\right) + \left(\frac{1-\nu_2^2}{E_2}\right)\right\}\right]$ where E_1 & E_2 are the elastic modulii and ν_1 & ν_2 are the Poisson's ratios of the two solid bodies in contact, η_0 - Viscosity of the fluid at atmospheric pressure, $\bar{u}$ - Mean entrainment velocity of the two surfaces in x-direction, R - Initial radius of the cylinder, α - Viscosity-pressure coefficient, h_0 - Oil Film thickness

On calculation for the condition of a 60 N load and a 0.11 m/s linear speed, which were used to simulate the boundary conditions, the oil film thickness was found to be 0.5 μm, which is much less than the roughness values of the surfaces in contact. This suggests clearly that the experimental conditions selected are simulating the boundary lubrication conditions. For comparison purposes, experiments were also conducted for bare Al shaft and Al plate for the industrial lubricant with additives for the boundary conditions.

Figure 5a compares the specific wear rates calculated for the bare Al with the base oil, industrial lubricant and the nanocomposite film-coated cylindrical shaft and the flat pin under the boundary lubricating conditions of base oil without any additives. It can be clearly observed that the wear rates of the (uncoated) bare Al shaft with the base oil and the industrial lubricant are much higher when compared to that of the nanocomposite-coated shaft case under the same test conditions with the base oil. For the nanocomposite- coated shaft, the data show the wear of the coating and hence we may say that there was zero wear of the Al shaft itself. The EDS analysis conducted on the nanocomposite film after 100 h of wear test is shown in Fig. 5c. The presence of the strong C peak and the absence of the Al peak verifies that the nanocomposite film did not peel off or wear off from the surface of the Al substrate, showing its effectiveness in protecting the Al surface of the shaft. Figure 5b gives the specific wear rates of the counterface Al flat plate when slid against the bare Al and the nanocomposite film-coated shaft, respectively, under the boundary lubrication conditions. It is observed that when the Al flat plate is slid against the bare Al cylindrical shaft with the base oil and the industrial lubricant, the specific wear rate of Al is much higher (more than three orders of magnitude) than when slid against the nanocompositecoated shaft. This can be mainly attributed to the excellent wear properties of the nanocomposite film with low friction and no adhesion with the bare Al plate surface. Sliding between two bare metals in the boundary lubrication regime produces severe wear because of the direct adhesive interaction between the surfaces. Metals are known to fail by scuffing when lubrication is not sufficient. Figure 5d, e and g shows the quality of the lubricating base oil before the test, after the test (100 h) for the bare Al and the nanocomposite-coated Al shafts, respectively. Figure 5f shows the quality of the industrial lubricating oil after a test of 100 h under the same conditions. It can be seen that the oil quality in the case of bare Al shaft has deteriorated considerably because of the oxidation and the generation of the wear debris due to the wear and tear caused during the test. The blacking sludge type of wear debris is typical of metal wear in insufficient lubrication. It is observed that the colour of the oil does not change in case of the nanocomposite-coated Al shaft due to the protection offered by the coating against any wear. No wear debris was observed in the oil after filtration which can be attributed to the excellent mechanical properties of the nanocomposite film and the strong bonding between the carbon nanotubes and the polymer matrix.

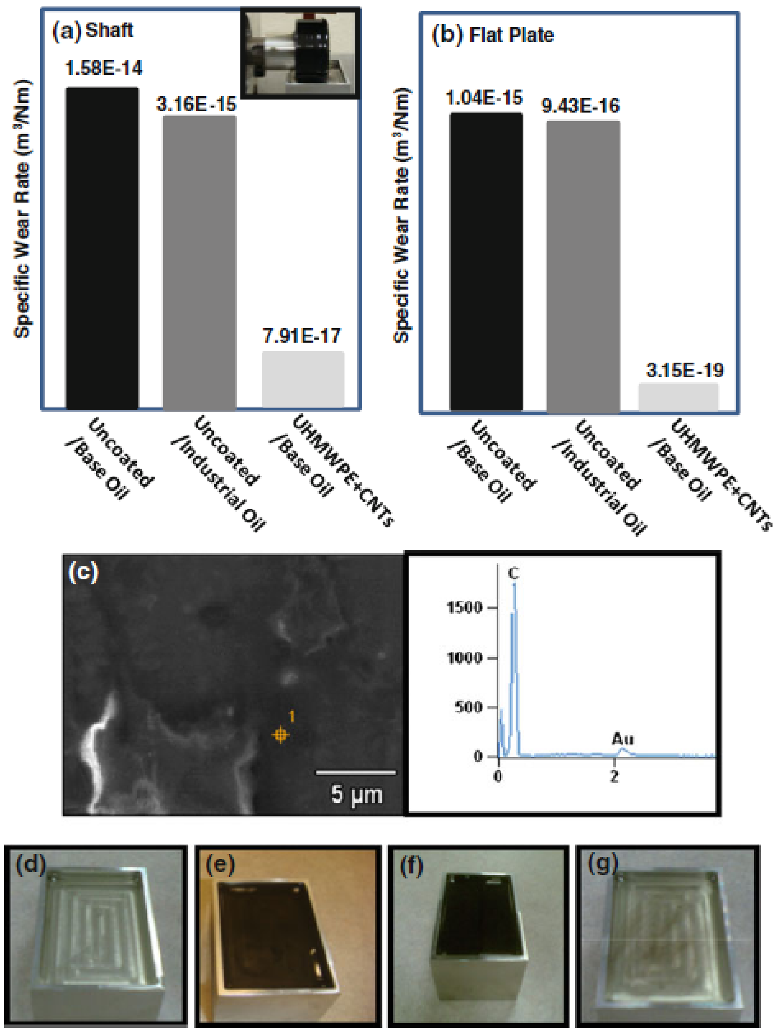

Fig. 5 **a** A comparison of the specific wear rates of the uncoated Al cylindrical shaft under the base oil and the industrial lubricant conditions and that of the nanocomposite coating under base oil lubrication under a load of 60 N and a linear speed of 0.11 m/s. **b** A comparison of the specific wear rates of the counterface Al flat pin under the base oil and the industrial lubricant conditions and that of the nanocomposite coating under base oil lubrication under a load of 60 N and a linear speed of 0.11 m/s. **c** EDS spectrum in the wear track of the nanocomposite coating after a wear test of 100 h under the base oil under a load of 60 N and a linear speed of 0.11 m/s. **d** Initial base oil quality. **e** Quality of the base oil after a wear test (100 h) of uncoated Al shaft under a load of ~60 N and a linear speed of 0.11 m/s. **f** Quality of the industrial oil after a wear test (100 h) of uncoated Al shaft under a load of 60 N and a linear speed of 0.11 m/s. **g** Quality of the base oil after a wear test (100 h) of nanocomposite-coated Al shaft under a load of 60 N and a linear speed of 0.11 m/s

Figure 6a–c shows the profiles of the wear scar on the flat plate as obtained from the optical profilometer, when slid against bare Al shaft under the base oil lubricated conditions. It can be observed that the counterface flat plate undergoes much wear mainly due to the absence of the oil film between the mating surfaces during the boundary lubrication. However, with a protective nanocomposite film on the cylindrical shaft no wear is observed on the counterface Al flat plate reiterating the effectiveness of the nanocomposite film in protecting the metal parts during the boundary lubrication as shown in Fig. 6d–f. Figure 7 shows a typical frictional graphs for the bare Al and nanocomposite film-coated shaft under the boundary lubrication conditions. Even though the average coefficient of friction in both the cases are nearly same as seen from the figure, a lot of wear is observed on the two mating surfaces in case of the bare Al shaft. The lubricating oil was completely contaminated with the wear debris in the case of uncoated shaft, as discussed above.

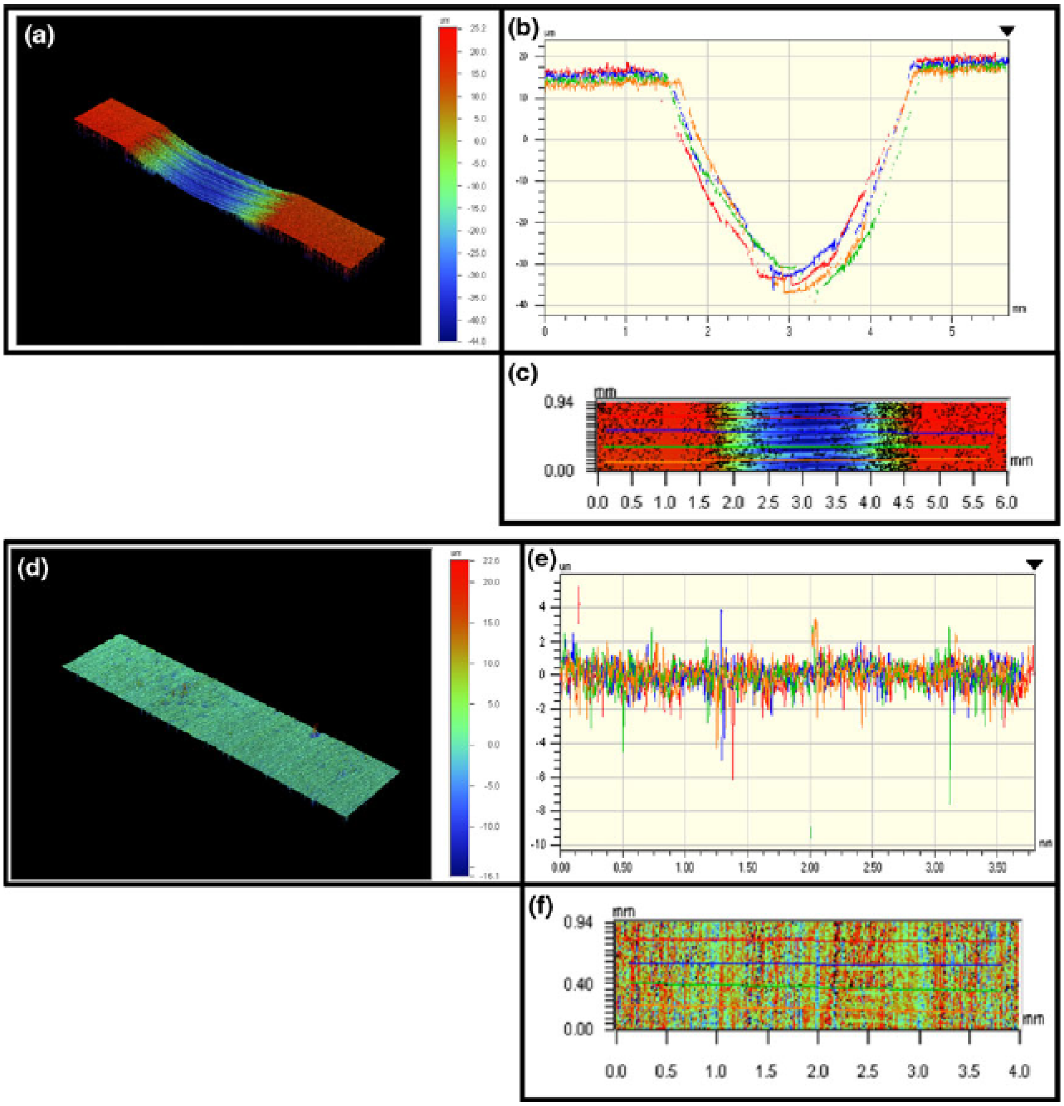

Fig. 6 3D profile, the actual profile and the 2D profile of the scar on the counterface Al flat pin after a wear test of 100 h with the base oil lubrication under a load of 60 N and a linear speed of 0.11 m/s when slid against **a–c** the uncoated cylindrical Al shaft, **d–f** the nanocomposite-coated cylindrical Al shaft

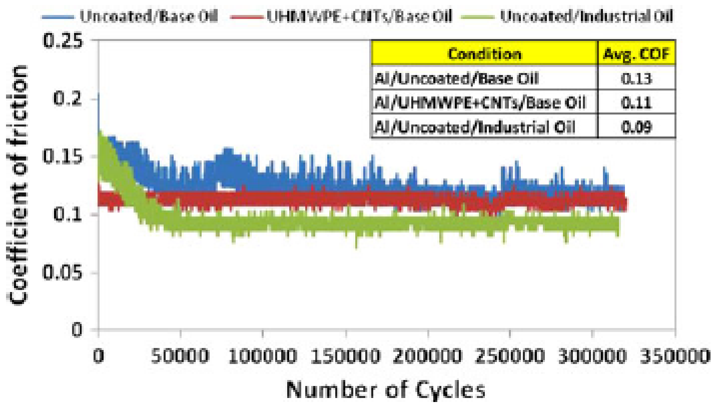

Fig. 7 A typical coefficient of friction curve for the uncoated/base oil, uncoated/industrial oil and UHMWPE + CNTs/base oil under a load of 60 N and linear speed of 0.11 m/s. Inset: comparison of the average coefficients of friction for the three cases

5.2.3 Evaluation of the Polymer Coatings in the Mixed Lubrication Regime

Wear tests were also conducted under the mixed lubrication conditions at a load of 45 N and a speed of 0.57 m/s to evaluate the effectiveness of the nanocomposite coatings in this regime. Basically, in the mixed lubrication regime, the two contacting surfaces are partially separated due to the thin oil film formation between them, thus reducing the amount of wear on the mating surfaces. In this regime the load is shared between the oil film formed between the surfaces and partially by the asperity contacts, thus leading to less wear. To verify our experimental parameters, the oil film thickness in this regime is also calculated by using the above-mentioned equation. The film thickness was found to be approx. 1.69 µm, which is comparable to the roughness of the coating, suggesting that it is the mixed lubrication regime [38]. It is observed that in this regime, the specific wear rates of the uncoated Al shaft (4.22 X 10^{-16} m^3/Nm) and the mating plate (6.65 X 10^{-17} m^3/Nm) are lower when compared to that during the boundary lubrication regime. However, in case of the nanocomposite coating no wear was observed on the wear track except for the flattening and smoothening of the coating as is evident from the FESEM images, 3D profile images from the optical profilometer and the EDS analysis as shown in Fig. 8. EDS in the wear track region showed no Al peak. Moreover, the colour of the lubricating oil turned blackish in case of the uncoated Al shaft due to the generation of the wear debris and oxidation, similar to what has been observed during the boundary lubrication tests as mentioned above. On the other hand, the oil remained uncontaminated and clear in case of the nanocomposite-coated Al shaft, again proving the effectiveness of the film in protecting the metal parts from wear and also from oxidation.

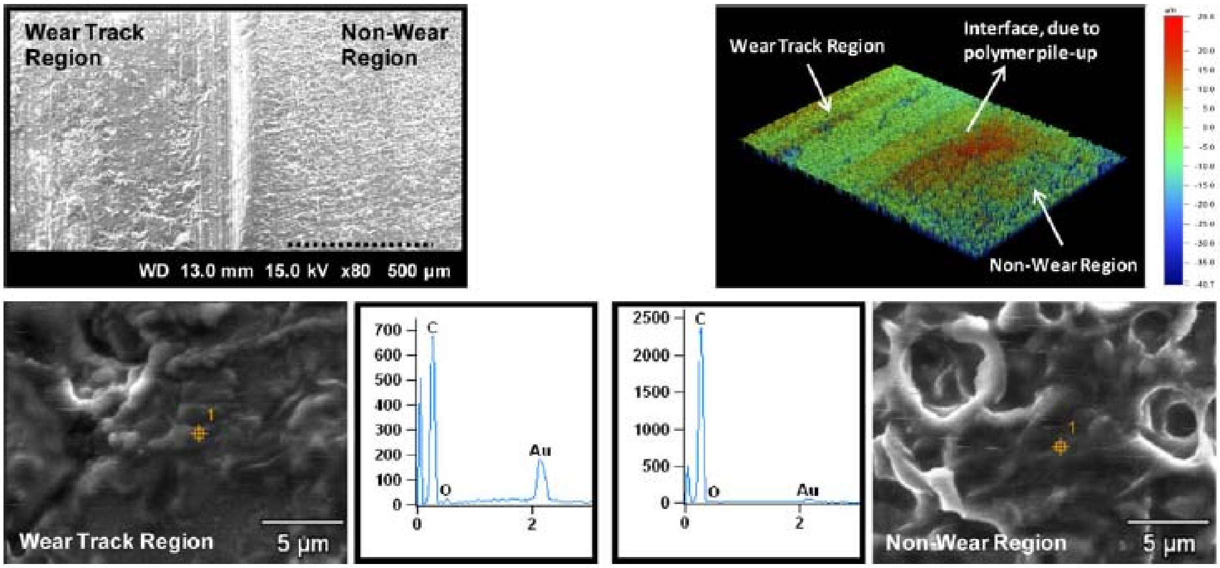

Fig. 8 FESEM image, 3D profile, EDS spectrums for the nanocomposite coating after a wear test of 100 h with a load of 45 N and a linear speed of 0.57 m/s under the base oil lubricating conditions

5.3 Nanoindentation Results

Nanoindentation tests were conducted to evaluate the effect of the lubricating base oil on the hardness and the elastic modulus of the nanocomposite film. Tests were carried out after the nanocomposite film had been subjected to a 100-h of wear test under the dry and boundary lubricating conditions. Table 2 lists the average values of hardness and elastic modulus of the nanocomposite film before and after the wear tests under lubricated conditions with the base oil for 100 h. It is observed that the base oil does not alter the mechanical properties of the nanocomposite film to any great extent. The reduction observed is the effect of the presence of lubricant in-between the indenter and the coating. The lubricant allows the indenter to penetrate slightly deeper and hence the measured hardness value is slightly low for lubricated coating. The currently measured difference is an indication of no reduction in the mechanical properties of the coating in the presence of oil.

Table 2 Comparison of the average values of hardness and elastic modulus of the nanocomposite coating before the test and after the test under the base oil lubrication

Condition	Hardness (MPa)	Elastic modulus (Gpa)
Dry	104 ± 8	2.56 ± 0.7
Lubricated	94 ± 6	2.16 ± 0.4

6 Conclusions

In this study, the effectiveness of the nanocomposite (UHMWPE ? 0.1 wt% CNTs) polymer film as a boundary lubricant has been evaluated under the base oil lubrication without any additive. The following conclusions can be drawn from this study:

- The addition of 0.1 wt% CNTs to the UHMWPE polymer improved the wear life of the coating from 250,000 cycles to more than 2 million cycles under dry sliding conditions against a bare Al flat plate.
- Under the severe boundary-lubrication condition, the nanocomposite polymer film is found to be very effective in protecting the mating surfaces from wear under the base oil lubrication without any additives.
- Minimal wear of the coating and no wear of the counterface metal was observed up to 2 million cycles of sliding in lubricated contact with the nanocomposite film.
- The mechanical properties of the nanocomposite film are not altered by the base oil even after a test duration of 100 h.
- The nanocomposite polymer coating as a boundary lubricant is found to be an effective way to reduce or eliminate the usage of harmful additives in the lubricating oils.

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