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Tribological studies of epoxy composites with solid and liquid fillers



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ABSTRACT

Epoxy-based composites are promising tribological coatings. The tribological properties of epoxy composites with filler materials such as graphene, graphite, and liquid lubricants (base-oil SN150 and perfluoropolyether) are studied. The composite coatings were applied on cylindrical steel surface and a steel ball was used as the counterface. Tests were conducted at 10 N normal load and 0.63 m/s linear sliding speed. Among all coatings, epoxy filled with graphene and SN150 lubricant provided the lowest coefficient of friction of 0.09 with wear cycles exceeding 200,000 and specific wear rate of $5.4 \times 10^{-7} \text{ mm}^3/\text{N-m}$. Speed effects on friction were also evaluated.

1. Introduction

Presently, there is a trend towards using lubricants without any additives (such as friction modifiers) that are harmful to the environment. Metals, such as steel, wear heavily if only base lubricant oil is used specially in boundary lubrication regime. Polymer-based coatings have been applied on steel surfaces which work well in both dry and base oil lubricated conditions [1]. Machine components can be protected by such tribological coatings. A suitable polymer coating provides low coefficient of friction (CoF), low wear and very good adhesion properties with many substrates [2]. There are many polymers such as epoxy, SU-8 (an epoxy-based polymer), PEEK, UHMWPE, PTFE, *etc.* which have been used as coatings to improve the tribological performances of solid surfaces [2–4]. They can work like an effective boundary lubricant, thus protecting the steel surfaces.

Epoxy resin is a thermoset polymer having a number of well-known advantages including high toughness and strength, adhesion, durability at low and high temperatures and thermal stability, high chemical resistance, low shrinkage and ease of fabrication [5–8]. Epoxy resins are widely used in applications ranging from electric and electronic systems to automotive parts, aircraft components, biocompatible implants, protective coatings, and adhesives [5]. Normally, epoxy is a poor tribological material. However, addition of suitable fillers such as graphene and liquid lubricants (such as base oil SN150) can enhance its performance with low coefficient of friction and high wear life [1]. Such kind of tribological bearing materials (with liquid fillers) successfully operates in the boundary to mixed lubrication regimes. Hence, a literature review on this type of lubrication and associated analysis are presented below.

Different micro/nano-filler have been added in epoxy and other polymers for tribological performance enhancement. Microencapsulated lubricant (70SN) was incorporated in epoxy by Guo et al. [9]. The results showed that at 10 wt% of the microcapsules the coefficient of friction was reduced from 0.56 to 0.14 and there was a reduction in the specific wear rate by two orders of magnitude. However, mechanically, the composite was weaker (flexural strength) by half at 10 wt% of the filler compared with the base polymer and also there was a tendency for the coefficient of friction and wear to increase beyond the optimum 10 wt% filler content. Similar work has also been reported by Khun et al. [10]. Sarvanan et al. [11] have used perfluoropolyether (PFPE) lubricant in the form of micro/nano sized droplets in SU-8 matrix reducing the steady-state coefficients of friction by ~6 times, and increasing the wear life by more than 10^4 times. It was shown that liquid lubricant-filled SU-8 provides lubrication by the mechanism of physical boundary layer. The friction and wear performances are largely unaffected by load, however, there is a limiting maximum speed beyond which physical boundary layer may become ineffective.

Surface modification by developing polymer brushes of alkyl methacrylates with hexyl, octadecyl and dodecyl side chain on silica and iron surfaces were carried out by Bielecki et al. [12]. The Stribeck curves were plotted for hexadecane, toluene and ethanol as lubricants between the polymer brushes which showed very low friction coefficient (~0.01) at low speed (0.1 m/s) which increased with speed. The study concluded that the increase in viscosity causes gradual increment of shear stress at the interface.

Sophie et al. have found that for monolayers of additives and friction modifiers, the coefficient of friction increases with velocity

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Table 1

Tensile properties and Vicker's hardness data for pure epoxy and its composites. All fillers, graphene, graphite, SN150 and PFPE were in concentration of 10 wt% in each case.

Material	Ероху			Epoxy/Graphene		Epoxy/Graphite	
Liquid filler material	none	PFPE	SN150	PFPE	SN150	PFPE	SN150
Young modulus GPa	0.815	0.687	0.716	0.832	0.848	0.755	0.838
Tensile strength MPa	40	40.571	41.53	38.331	43.96	28.903	32.64
Hardness MPa	215	134.1	132.3	204.3	157.4	144.6	141.8



Fig. 1. Schematic diagram of the ball-on-cylinder tribometer.

under boundary lubrication regime [13]. They observed that the saturated friction modifiers (such as stearic acid), which are adsorbed on the surface in orderly closed-packed configuration, show low friction whereas the unsaturated friction modifiers (such as oleic acid and elaidic acid) exhibit high friction due to not closely-packed monolayer.

The frictional behavior of automotive transmission fluids for wet clutch in which regimes of boundary lubrication occur over the complete sliding velocity range, was studied by Ingram et al. [14]. Friction modifiers and additives (such as 12-hydroxystearic acid, C18-acid and C18-amine) provide low friction at low velocities (less than 0.01 m/s), and friction increases with speed. They also reported that the functional polar groups such as –OH and –COOH displayed a trend of a rapid increase in friction with increasing speed and at high speeds there is certain fall due to insufficient time to return to their original state of bonding between friction modifiers and the pad surface.

The frictional behavior of silica surfaces with and without absorbed brush like copolymer of poly (L-lysine)-*graft*-poly (ethylene glycol) (PLL-*g*-PEG) and poly (L-lysine)-*graft*-dextran (PLL-*g*-dextran) in aqueous solution were studied as a function of shear viscosity by Prathima et al. [15] with the help of colloidal-probe lateral force microscopy. Nano-scale Stribeck curves were obtained for bare silica in selected solvents which described the effect of solvent viscosity on measured frictional force. Under the boundary lubrication regime, the adsorbed hydrated ions acted as a surface-solvating thin film, preventing direct physical contact. It was also found that polymer brushes reduce the friction for a specific solvent mixture. Further, solvated polymer brushes shift the hydrodynamic lubrication regime to the left towards smaller values of the product, sliding speed×viscosity (Uη).

In the boundary lubrication regime (i e. low value of Sommerfeld number), the lubricant film thickness is lower than the surface roughness, and the coefficient of friction lies between 0.08 and 0.12. The coefficient of friction was found to be independent of normal load [16]. The lubrication regime of ball bearings and gears were found to be in the elasto-hydrodynamic lubrication regime only at high and moderate speeds and fluid film thickness gives a trend with $(U\eta)^{0.7}$. In this regime of lubrication, the coefficient of friction lies between 0.02 and

0.10, and it is independent of viscosity and depends upon molecular structure of the lubricant [17].

Earlier study has shown that in the *in situ* lubrication case, there is strong dependence of coefficient of friction on the sliding speed but there is minimum effect of the normal load within a range [18]. The *in situ* lubrication is indeed a case of mixed lubrication for which two analyses have been provided. Albertson [16] proposed that for the lubricants with additives, the boundary film formation is a diffusion controlled phenomenon (based on Eyring's rate of diffusion [19]) and hence the coefficient of friction will depend upon the sliding speed.

It was presented by Sophie et al. [13] that in the boundary and mixed lubrication regimes the interfacial shear stress is a function of the sliding speed. The analysis uses the Eyring [19] equation for activated slip model. It is based on the principle that when one layer of molecules slips over another, there is an activation energy needed for this slip to overcome the energy barrier. The values are different in forward and backward directions. The rates of slip depend upon the applied shear stress and the thermal fluctuations. Using this approach they have shown that the net velocity for slip is an exponential function of the shear stress. Thus, upon taking logarithm on both sides, the following relation is obtained [13,18],

$$\tau = (kT/\phi) \ln\left(\frac{v}{v_0}\right) + \frac{1}{\phi} (E + P\Omega)$$
(1)

where τ is the shear stress, v is the relative velocity, v_o is a reference velocity, ϕ is the shear activated volume, Ω is the pressure activation volume, T is the absolute temperature, k is the Boltzmann constant, E is the activation energy and P is the hydrostatic pressure. The full derivation of Eq. (1) is given in Ref. [13].

Thus, the relation between v and τ can be given as follows;

$$\tau = \tau_{\rm l} + \theta \ln(v) \tag{2}$$

where,

$$\tau_{\rm l} = \frac{1}{\phi} (E + P\Omega - kT ({\rm In} v_0)); \ \theta = \frac{kT}{\phi};$$

where τ_1 and θ are constants for the given boundary layer. The coefficient of friction is very much influenced by interfacial shear strength [18]. Eq. (2) was also derived by Briscoe and Evans [20] which also described the experimental data for monolayers very well. If it is assume that for a fixed applied load, the contact area and thus the pressure is constant, Eq. (2) can be re-written for the boundary friction as,

$$u_b = a + a_1 \ln v \tag{3}$$

where a and a_1 are constants for a set of load and temperature.

For the boundary lubrication by mono and multilayers of carboxylic acid, Briscoe and Evans [20] also proposed the relations for shear stress as functions of constant pressure, P, and temperature, T, which are given as;

$\tau = \tau_2 + \alpha P$	(At constant temperature and velocity)	(4)
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$$\tau = \tau_3 - \beta T$$
 (At constant pressure and velocity) (5)

where α , β , τ_2 , τ_3 are constants for a given lubricant.

The wear and lubrication mechanisms of SU-8 filled with PFPE (Z-



Fig. 2. FESEM images of the cross-sections of the coatings.

dol) droplet were investigated by Saravanan et al. [18] under different regimes of lubrication. The lubrication mechanism was explained by studying the variation of coefficient of friction with the sliding velocity trends by dividing it in three zones.

From the above literature survey, it can be concluded that there is a strong dependence of the CoF on the speed, whereas CoF is mostly independent of normal load. The mixed lubrication is a possible mechanism of lubrication for liquid-filled polymer coatings where lubrication is continuously provided *in situ*. In the present study, we will compare the CoF with respect to speed and normal load for the epoxy composites filled with two solids (graphene and graphite) and two liquid (SN150 and PFPE) lubricants.

2. Experimental procedure

2.1. Materials

Epoxy and its composites filled with liquid lubricants (SN150 or PFPE) and graphene or graphite particles were coated onto D2 tool steel cylindrical shaft (diameter = 40 mm). The thickness of the coating was in the range of 50–60 μ m. Base-oil SN150 (Indian Oil Corporation Limited Faridabad India) of Group-I with viscosity 24.25 cP (at 40 °C) and PFPE (commercial name Fomblin Y, supplied by Sigma Aldrich, India) with viscosity of 43.38 cP (at 40 °C) were used. Graphene with particle sizes <100 nm was supplied by Reinste Nano Ventures Pvt



Fig. 3. Stribeck curve for (a) epoxy/10 wt% graphene/10 wt% SN150 and (b) epoxy/10 wt% graphene/10 wt% PFPE composite tested at a normal load of 10 N for a fixed 5000 sliding cycles. Zone 1 and Zone 2 are two regimes with different frictional behaviors. Zone 1: CoF increases steeply with Sommerfeld number (a) 0–11 and (b) 0–19. Zone 2: CoF increases marginally for (a) 11–52 and decreases marginally for (b) 19–119.

Ltd, India, and graphite with particle sizes $< 20 \ \mu m$ was purchased from Sigma Aldrich, India. The epoxy used was Araldite AY 103 with hardener HY 951, supplied by Huntsman Advanced Material Pvt. Ltd. Steel ball (SAE 52100 with hardness of 58 HRC) of 4 mm diameter and roughness 50 nm was used as counterface for all tribological tests.

2.2. Sample preparation

D2 tool steel cylindrical specimen of diameter ~40 mm and width ~12 mm was prepared by turning and then grinding the surface till the roughness of Ra~0.40 μ m. The surface was cleaned with acetone, airdried and treated with air plasma [1]. Air plasma cleaning was carried out on steel surface to remove any organic impurity and to generate hydroxyl groups on the substrate which increase the adhesion of the coating to the substrate. The filler materials were added into liquid monomer epoxy and stirred thoroughly using ultrasonication. After this, the hardener was mixed and the air bubbles were removed by exposing the mixture to vacuum. Four different types of composites were prepared:

- (i) Epoxy/graphene (10 wt%)/SN150 (10 wt%) (named as E/Gn/ SN150).
- (ii) Epoxy/graphene (10 wt%)/PFPE (10 wt%) (named as E/Gn/ PFPE).
- (iii) Epoxy/graphite (10 wt%)/SN150 (10 wt%) (named as E/Gt/ SN150).
- (iv) Epoxy/graphite (10 wt%)/PFPE (10 wt%) (named as E/Gt/PFPE).

The steel surfaces were coated with epoxy composites by a labfabricated 'dip and rotate' coating machine and then by rotating the coated shaft at 100 rpm for 4 h in order to distribute the epoxy composite uniformly over the shaft while it air-cured. The coatings were cured initially at room temperature for 16 h followed by thermal curing at 80 °C for 4 h. The final coating thickness varied between ~50 and 60 μ m. The samples were then stored in a desiccator before any further use.

2.3. Material characterization of epoxy composites

Mechanical properties such as tensile strength and modulus of elasticity of the polymer composites were measured using tensile tests and the hardness was measured by Vickers hardness tester.

2.3.1. Tensile strength and modulus of elasticity

ASTM standard D638 test samples were prepared by casting in a mould of dimensions 3 mm×3.9 mm cross-section with a gauge length of 10 mm [1]. The curing process followed was same as explained for the coating on the steel shaft. Tensile tests of composites were performed using a universal testing machine with a cross-head speed of 0.1 mm/min. The moduli of elasticity and tensile strengths of epoxy composites filled with liquid lubricants and graphene or graphite particles are given in Table 1. Each datum represents an average of three repeated tests. These observations show that there is some decrement in the tensile strength on adding graphite with liquid filler whereas with graphene there is an increment by ~10%. The modulus of elasticity is increased for both graphene and graphite additions. However, this increase in the elastic modulus is more for graphene than for graphite. In general, graphene is more effective in improving the mechanical properties of epoxy which indicates better bonding between the two because of smaller size of the graphene particles.

2.3.2. Hardness

Hardness of the composites was evaluated by Vickers hardness tester [1]. The hardness values of different composites are also presented in Table 1. The data reported are averages of ten measured values on at least two different specimens.

2.4. Tribological test

Friction and wear tests were performed using lab-fabricated ballon-cylinder tribometer setup (Fig. 1). Photo of the experimental set-up was shown in our earlier publication [1]. The polymeric coatings were coated on the cylinder outer surface. The ball used was bearing steel (SAE 52100) of diameter 4 mm. The tests were conducted at the normal load of 10 N and at different rotational speeds of 10, 20, 50, 100, 200, 300, 600, 1000 and 1200 rpm. The linear sliding speed range was varied from 0.021 m/s to 2.5 m/s. In order to understand the load effect, the tests were also performed at a speed of 0.63 m/s and three different normal loads (3, 6 and 10 N). All tests were conducted at room temperature (25 ± 2 °C) and relative humidity of $45 \pm 5\%$. The steady-state coefficient of friction (CoF) was estimated by taking average of the last 1000 values before coating failed. Sommerfeld number $(\eta V/P)$ was also calculated in order to plot the Stribeck curve for two composites which are epoxy/graphene/SN150 and epoxy/ graphene/PFPE. In order to calculate the volumetric wear rate, the wear track width and depth profiles were measured by using 3D optical profiler (Contour GTK, Bruker, USA). Images of worn surfaces on the cylindrical and ball surfaces were taken by optical microscope.

2.5. Surface characterization of epoxy composites

2.5.1. Optical and scanning electron microscopy

The worn surfaces of specimen sample and ball were observed by Digital Microscope (Dino-lite, Kontrelek Instruments, India) to analyze the wear behavior of each sample. This is a portable type microscope with 270-480 X magnification. The images of tested ball were also analyzed by Confocal Microscope. Field Emission Scanning Electron Microscopy (FESEM) was carried out on EIGMA, Zeiss, USA FESEM machine. The samples were gold coated using a sputter coater (SC7620-CF, Quorum Laughton Lewes) prior to FESEM imaging. SEM images of the cross-sections of the four composites E/Gn/ SN150, E/Gn/PFPE, E/Gt/SN150 and E/Gt/SN150 are shown in Fig. 2. It is seen in these images that the volume of SN150 is much larger than that of PFPE. Also, between graphene and graphite based composites, the lubricant droplets are larger and more in volume in the case of graphene than in the case of graphite presence. These differences will be discussed in later sections.

2.5.2. 3D optical profiler analysis

3D optical profiler (Contour GTK, Bruker, USA) was used for wear track profile measurements. The cross-sectional area of the wear track was calculated by integrating the width and depth profiles which was then multiplied by the total track length to obtain the wear volume. The specific wear rate (W_{sp}) was calculated using the following relation [8],

$$W_{sp} = \frac{V}{LD} \text{ mm}^3/\text{N m}, \tag{6}$$

where V is the wear volume, L is the normal load and D is the total sliding distance.

2.5.3. Atomic force microscopy

Atomic force microscope (XE7, Park System, South Korea) was used for the surface topography of the epoxy composites. The AFM imaging of the specimen surfaces and the wear tracks was carried out to understand material surface topography before and after the wear process.

3. Results and discussion

3.1. Friction results and stribeck curve

Fig. 3 presents the steady-state coefficient of friction (CoF) values versus Sommerfeld number for the epoxy/graphene composites with (a) 10 wt% SN150 and (b) 10 wt% PFPE. The Sommerfeld number was calculated as $\eta v/P$, where η is the viscosity of the liquid filler, v is the sliding speed in m/s and P is the normal load (10 N). The coefficient of friction was inspected for a fixed 5000 sliding cycles for different Sommerfeld numbers. The plot is divided into two different zones based on their frictional behavior with respect to the Sommerfeld number, Zone 1 and Zone 2, which represent an abrupt change in the coefficient of friction increased very steeply from 0.04 to 0.06, while in zone 2, it was nearly constant (0.06–0.07) for SN150. In the case of PFPE, the CoF in Zone 1 increases from 0.06 to 0.12 and in Zone 2 decreases from 0.12 to 0.10. The mechanisms responsible for frictional

behavior in Zone 1 and 2 are explained in the next section.

Table 2 presents optical images of coating worn surfaces and the ball surfaces. These images show less amount of lubricant transfer onto the ball in Zone 1. In Zone 2, there is less lubricant on the ball and the composite surface (v=0.63 m/s). However, at v=2.51 m/s the amount of lubricant increases at the interface. This somewhat correlates with the CoF which stabilizes at higher sliding speed or reduces marginally.

3.1.1. Zone 1 mechanism

In Zone 1, the coefficient of friction rises sharply as the Sommerfeld number is increased. This rise is in contrast to the typical Stribeck curve in which the CoF decreases in value as Sommerfeld number is increased.

A schematic of the coating cross-section with the bonded and mobile lubricant is shown in Fig. 4. There is presence of lubricant liquid droplets in the bulk and at the sliding surface; there is mobile lubricant presence due to the opening up of those droplets. In the beginning of the sliding process, the bonded and mobile lubricant molecules present on the surface provide sufficient lubrication [12,15], keeping the CoF in the range of 0.042. The trapped droplets of the lubricant are quickly released in the beginning of the sliding process which maintains low shear stress at the interface. The low CoF condition is maintained for 5000 cycles and above because of the *insitu* supply of lubricant.

It is seen that with increase of sliding velocity, lubricant displacement increases from contact point. At low sliding speed, a balance is maintained between the displacements of lubricant from the wear track and re-flow. But at higher speed, the displaced lubricant is not quickly available on the wear track due to insufficient time leading to lubricant starvation [16]. The repeated movement of lubricant from wear track causes asperity contact, and the coefficient of friction increases, which leads to wear. The images of the counterface ball after wear test and the worn surfaces also support the proposed mechanism for displaced lubricant as given in Table 2. The images of the counterface ball show the presence of lubricant on their surfaces which initially increases with increase of speed and also some amount of wear debris is present on the ball surface.

3.1.2. Zone 2 mechanism

Zone 2 shows a mechanism where lubricant is mixed with the wear debris in the form of slurry. The slurry effectively provides lubrication. The CoF is maintained at constant value of approximately 0.07–0.08 for SN150 filled composites. The CoF decreases from 0.12 to 0.09 for the PFPE-filled composites as the Sommerfeld number is increased from 15 to 120.

These observations clearly show that there is strong influence of the *in-situ* lubricant present in the matrix of epoxy. The lubrication regime is that of mixed lubrication type where both liquid and solid interactions play their parts. It is seen that for liquid-filled composites, the slurry of lubricant and initial wear debris also play an important role in maintaining low CoF at high speed. In fact CoF decreases for epoxy/graphene/PFPE when the Sommerfeld Number is increased (Fig. 3(b)).

3.2. Effects of speed on the coefficient of friction

As the liquid filler (SN150 and PFPE) is added in epoxy composites (epoxy/graphene and epoxy/graphite) the coefficient of friction goes down drastically and load bearing capacity also increases. Fig. 5(a) and (b) presents the coefficient of friction versus sliding velocity for epoxy/ graphene composite with the liquid fillers SN150 and PFPE, respectively, for three different loads. From Fig. 5(a) it is observed that the variation of coefficient of friction with sliding velocity is nearly same at the loads of 3 N, 10 N and 12 N. At lower speed, the coefficient of friction is low (0.04–0.06) and increases steeply with velocity up to

Table 2

Optical images of the ball contact surface and the corresponding wear tracks for epoxy/graphene (10 wt%)/SN150 (10 wt%) composite coating at the steady-state of the sliding process. They are typical examples of the interfaces in Zone 1 and Zone 2 regimes. Scales are provided in each image.

Speed (m/s)	CoF	Ball Images	Worn Surfaces
Zone 1 0.02	0.042	200 µm	<u>100 μm</u>
0.42	0.062	200 up	<u>100 μm</u>
Zone 2			
0.63	.066	200 µm	<u>100 µm</u>
2.51	0.065	<u>200 µm</u>	100 µm



Fig. 4. Possible sequence of lubrication mechanisms at the ball-surface interface during tribological test and lubricant distribution in composite.

0.42 m/s and then becomes nearly constant (CoF~.09) in the velocity range of 0.42 m/s-2.51 m/s for all composites. The epoxy composites filled with SN150 shows lower coefficients of friction (0.04–0.1) as compared to those for PFPE (CoF 0.06–0.17). In Fig. 5(b), the variation of the coefficient of friction at different loads (3 N, 10 N

and 12 N) shows same behavior with velocity but has very different coefficients of friction. At 10 N normal load, the coefficient of friction for epoxy/graphene/PFPE shows the lowest value (0.06-0.11) whereas at other loads the values are much higher. For PFPE, in general for all loads, slight reduction in the CoF at high speeds is observed. However,



Fig. 5. Variation of coefficient of friction with sliding velocity of epoxy/graphene composites with liquid lubricant coated on cylindrical surface of steel for three different loads (a) epoxy/graphene/SN150, (b) epoxy/graphene/PFPE. Each filler concentration was 10 wt%.



Fig. 6. The effect of load on coefficient of friction for epoxy composite with liquid lubricant coated on steel cylinder and tested on ball. Each filler concentration was 10 wt%.



Fig. 7. Shear stress (τ) versus ln(v) plot for (a) epoxy/graphene/SN150 and (b) epoxy/graphene/PFPE composites, tested at 10 N load with various sliding speed for 5000 no. of cycles. The curve was fitted to Eq. (3) and the values of τ_1 and θ were calculated from the intercept and slope, respectively. Each filler concentration was 10 wt%.

the CoF values for PFPE composites are higher in comparison to those for SN150 composites. It appears to be the effect of the volume of the lubricants in the composites. SN150 is less dense (density= 840 kg/m^3)

in comparison to PFPE (density= 1810 kg/m^3) and hence, the volume of SN150 is nearly double in the composite for the same wt%. Hence, more volume of SN150 liquid lubricant is present at the interface. With

lower viscosity of SN150, it is able to form much more lubricating slurry at the interface at higher sliding speeds. Hence, SN150 is able to provide lower CoF in comparison to that of PFPE at all sliding speeds.

3.3. Effects of load on the coefficient of friction

Fig. 6(a) and (b) present the initial and steady-state coefficients of friction of the coatings at different applied normal loads for the same linear speed of 0.63 m/s (300 rpm). For all composites, as the load increases, the initial coefficient of friction also increases. For epoxy/ graphene/SN150 the initial coefficient of friction is 0.04 at 3 N load and 0.08 at 10 N load, which are the lowest values amongst all epoxy composites with liquid fillers. It is found that the initial and steadystate coefficients of friction for PFPE are higher than those of SN150 in their composite forms. As explained before, the volume of SN150 was nearly twice that of PFPE because of density difference. This can result in large volume of SN150 lubricant present at the interface and hence low CoF. Another reason could be because of viscosity difference. PFPE has viscosity of 43.38 cP in comparison to 24.25 cP for SN150. Low viscosity fluid can provide low coefficient of friction. The steady-state coefficient of friction for Epoxy/graphene/SN150 composite is minimum (0.08) at lower loads (3 N and 6 N) and increases to 0.10 at 10 N load. Both for SN150 and PFPE cases, it is found that composites with graphene have lower CoF in comparison with that for the composite with graphite particle. Observing Fig. 2, it can be seen that the lubricant droplets are more in number in the case of graphene-based composite than in the case of graphite-based composite. In order to see the difference in the interaction between liquid lubricants and the filler particles, oil droplet contact angle was measured for each powder using the lubricants as the droplets. The contact angle of SN150 on graphene was measured as 47° in comparison to 28° on graphite. The contact angle of PFPE was measured as 73° on graphene in comparison to 27° on graphite. The experimental errors for all measurements were within \pm 1°. These data indicate that, in general, graphene is oliophobic than graphite. This property of graphene renders graphene-based composite with higher amount of free or mobile lubricant which helps in reducing friction. Graphite is oliophilic leading to physical absorption of the lubricant molecules much faster. Hence, in relative terms, graphenebased composite show low coefficient of friction for both the lubricants in epoxy. It will be shown in latter section that epoxy/Gn/SN150 has the lowest wear rate at all loads when compared to all other composites. At 10 N load, all composite coatings survive 200,000 no. of cycles except epoxy/PFPE.

3.4. Shear stress

Fig. 7(a) and (b) present the shear stress (τ) as a function of ln(v) plots for epoxy/graphene/SN150 and epoxy/graphene/PFPE composites, respectively, tested at the normal load of 10 N and at different sliding speeds for 5000 no. of cycles. The shear stress is calculated by assuming the contact area to be the Hertzian contact and the shear stress of interface is CoF times the pressure applied (Supplementary information, S1, provides the details). The data are fitted to Eq. (3) which is given as follows-

$\tau = \tau_1 + \theta \ln V$

The values of τ_1 and θ are calculated for epoxy/graphene/SN150 as 0.00758 GPa and 0.00565, respectively, and for epoxy/graphene/PFPE as 0.02279 GPa and 0.00358, respectively. There is an excellent fit of the data to this equation proving that the lubrication mechanism is in the mixed lubrication regime as proposed by Spikes [17]. The data also validate the relation given earlier by Briscoe and Evans [20] for monolayers of carboxylic acids and their soaps. In an earlier work [18], this equation was found to fit the experimental data for a SU-8 (epoxy type molecule) polymer matrix and functionalized PFPE (Z-dol) liquid filler composite. However, the curve fitting parameters were found to be different for different regimes. Hence, such differences are possible for different combinations of matrix and the liquid fillers.

3.5. Wear analysis

Wear performances of the coatings were evaluated by conducting the sliding tests at the maximum normal load of 10 N for all composites. After this, the wear rate was calculated by measuring the wear track profiles on 3D Optical Profilometer. Wear life was also observed in terms of the number of cycles for which the CoF remained at a low steady-state value. Failure of the coating was defined as the point when the CoF rose sharply (above 0.3) or became fluctuating. Fig. 8(a) presents plots of coefficient of friction as a function of the number of cycle at 10 N load and 0.63 m/s linear sliding speed for epoxy composites with liquid fillers. From this figure it can be observed that epoxy/PFPE and epoxy/graphite/PFPE fails very early as compared to other composites. It is clear from these data that epoxy/PFPE coating is much poorer in wear life compared with the other composites at different loads and sliding velocities tested. At 3 N and 6 N normal loads, wear lives of all the composites with liquid filler are more than 200,000 no. of cycle. Further, epoxy/graphite/PFPE coating gives poor wear-life at 10 N load and 0.63 m/s speed due to delamination of the coating. Based on the failure definition ($\mu \ge 0.3$), epoxy composites filled



Fig. 8. (a) Wear life as a function of number of cycle for sliding speed of 0.63 m/s (300 rpm) and 10 N load (b) Specific wear rate variation with load at 0.63 m/s (300 rpm) speed, for composites with liquid lubricant in dry test condition. Each filler concentration was 10 wt%.



Fig. 9. AFM images of original and worn surfaces of epoxy/graphene/SN150 (E/Gn/SN150) and epoxy/graphite/SN150 (E/Gt/SN150) composites. These composites showed the least steady-state coefficients of friction and minimum wear rates.

with SN150 do not fail till 200,000 no. of cycle. The experiments were stopped at 200,000 cycles due to long test duration. At 0.63 m/s (300 rpm) sliding velocity and 10 N load, all samples survived except epoxy/PFPE which failed very early within few 100 s of cycles and epoxy/graphite/PFPE coating which failed at nearly 70,000 no. of cycle.

In Fig. 8(b) specific wear rates $(mm^3/N-m)$ are plotted as a function of normal load for 0.63 m/s (300 rpm) sliding speed. It is found that epoxy/graphite/PFPE coating shows the highest wear rate at 10 N load. The wear rate of epoxy/PFPE coating is much higher (311.95×10⁻⁷ mm³/N-m) than those of composite coatings of epoxy/ graphite and epoxy/graphene combined with liquid lubricant filler. Hence, the datum for epoxy/PFPE is not included for 10 N normal load. Wear rates for the epoxy/graphene/SN150 composites remain nearly zero at low loads (3 N and 6 N) and gives lowest value than all other composites at the maximum load of 10 N. Epoxy/graphite/ SN150 also shows very low wear rate even at the highest load of 10 N. For all composites, the rate of change of wear rate follows different trend below 6 N normal load and above, except for Epoxy/ SN150 composite, in which case there is sharp increase in the wear rate beyond 6 N load. The composites with graphene nano particles and liquid filler have the best wear resistance. Fig. 9 provides AFM images of the unworn (original) and worn surfaces for two composites Epoxy/ graphene/SN150 and Epoxy/graphite/SN150. Whereas the original surface is very smooth, the worn surfaces show many pillars which tend to reduce the contact area which may also contribute to their excellent tribological performance in addition to the other effects mentioned earlier.

4. Conclusions

Coated samples of epoxy composites (with 10 wt% of graphene or graphite particles) with liquid lubricant fillers (10 wt% of SN150 or PFPE) were tested for tribological performance under dry sliding condition. The counterface was 4 mm diameter steel (SAE 52100) ball.

The sliding velocity and normal load were varied during the tribological tests. The conclusions drawn are as follows:

- 1. The composites filled with liquid lubricant coated on D2 steel act as self-lubricating layer with drastically reduced coefficient of friction (2 times reduction over the sample without liquid filler) and low wear rate.
- 2. The coefficient of friction increases with increase of sliding velocity initially, and after a speed of 0.42 m/s becomes nearly constant for the case of SN150. There is a decreasing trend for CoF of the composite with PFPE beyond a critical sliding speed.
- 3. Among all composites, the epoxy/SN150 gives lowest CoF (0.045) but at high load epoxy/graphene/SN150 shows the lowest coefficient of friction.
- 4. The wear rate for epoxy/graphene/SN150 is very low $(2.5 \times 10^{-7} \text{ mm}^3/\text{N-m})$ at 10 N load and nearly zero at low load of 3 N. This performance is followed by epoxy/graphite/SN150 which gives wear rate of $5.4 \times 10^{-7} \text{ mm}^3/\text{N-m}$ at 10 N load.

Overall, liquid-filled epoxy-based composites are very suitable as tribological coatings for load bearing applications in journal bearings, engine piston rings *etc.*

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.triboint.2016.09.010.

References

- V. Kumar, S.K. Sinha, A.K. Agarwal, Tribological studies of epoxy and its composite coatings on steel in dry and lubricated sliding, Tribol Mater Surf Interface 9 (2015) 144–153.
- [2] M.A. Samad, S.K. Sinha, Nanocomposite UHMWPE–CNT polymer coatings for boundary lubrication on aluminium substrates, Tribol Lett 38 (2010) 301–311.
- [3] X.Z.K. Loy, S.K. Sinha, Lubrication of polyether ether ketone (PEEK) surface by liquid ultrathin films for high wear durability, Wear 296 (1-2) (2012) 681-692.
- [4] R.A. Singh, N. Satyanarayana, S.K. Sinha, Surface chemical modification for exceptional wear life of MEMS materials, AIP Adv 1 (2011) 042141.
- [5] B. Bilyeu, W. Brostow, K.P. Menard, Epoxy thermosets and their applications I: chemical structures and applications, J Mater Ed 21 (1999) 281–286.
- [6] B. Bilyeu, W. Brostow, K.P. Menard, Epoxy thermosets and their applications II. Thermal analyses, J Mater Ed 22 (2000) 107–130.
- [7] C.A. May, Epoxy resins: 'chemistry and technology', Marcel Dekker, New York, 1988.
- [8] B. Bilyeu, W. Brostow, K.P. Menard, Determination of volume changes during cure via void elimination and shrinkage of an epoxy prepreg using a quartz dilatometry cell, Polimery 46 (2001) 799–802.
- [9] Q.B. Guo, K.T. Lau, B.F. Zheng, M.Z. Rong, M.Q. Zhang, Imparting ultra-low

friction and wear rate to epoxy by the incorporation of microcapsulated lubricant, Macromol Mater Eng 294 (2009) 20–24.

- [10] N.W. Khun, H. Zhang, J.L. Yang, E. Liu, Tribological performance of silicone composite coatings filled with wax-containing microcapsules, Wear 296 (2012) 575–582.
- [11] S. Prabakaran, N. Satyanarayana, S.K. Sinha, Self-lubricating SU-8 nano-composites for microelectromechanical systems applications, Tribol Lett 49 (2013) 169–178.
- [12] R.M. Bielecki, M. Crobu, N.D. Spencer, Polymer-brush lubrication in oil: sliding beyond the stribeck curve, Tribol Lett 49 (2013) 263–272.
- [13] C. Sophie, J. Green, L. Gordon, D. Atkinson, H.A. Spikes, On the increase in boundary friction with sliding speed, Tribol Lett 48 (2012) 237–248.
- [14] M. Ingram, J. Noles, R. Watts, S. Harris, H.A. Spikes, Frictional properties of automatic transmission fluids: part II-origins of friction-sliding speed behavior, Tribol Trans 54 (2011) 154–167.
- [15] C.N. Prathima, N.R. Shivaprakash, Rosa M. Espinosa-Marzal, N.D. Spencer, Exploring lubrication regimes at the nanoscale: nano tribological characterization of silica and polymer brushes in viscous solvents, Langmuir 29 (32) (2013) 10149–10158.
- [16] C.E. Albertson, The mechanism of anti-squawk additive behavior in automatic transmission fluids, ASLE Trans 6 (1963) 300–315.
- [17] H.A. Spikes, Mixed lubrication-an overview, Lubr Sci 9 (1997) 221-253.
- [18] P. Saravanan, S.K. Sinha, S. Jayaraman, H.M. Duong, A comprehensive study on the self-lubrication mechanism of SU-8 composites, Tribol Int 95 (2016) 391–405.
 [19] H. Eyring, Viscosity, plasticity, and diffusion as examples of absolute reaction rates,
- [19] H. Eyring, viscosity, plasticity, and dimusion as examples of absolute reaction rates, J Chem Phys 4 (1936) 283–291.
- [20] B.J. Briscoe, D.C.B. Evans, The shear properties of Langmuir–Blodgett layers, Proc R Soc Lond A 380 (1982) 389–407.