Lubrication of dry sliding metallic contacts by chemically prepared functionalized graphitic nanoparticles

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Abstract: Understanding the mechanism of precision sliding contacts with thin, adherent solid nano lubricating particle films is important to improve friction and wear behavior and ensure mechanical devices have long service lifetimes. Herein, a facile and multistep approach for the preparation of graphene oxide (GO) is presented. Subsequently, surface modification of as-synthesized GO with octadecyl amine (ODA) is performed to prepare hydrophobic GO-ODA and with 6-amino-4-hydroxy-2-naphthalenesulfonic acid (ANS) to prepare amphoteric GO-ANS through a nucleophilic addition reaction. X-ray diffraction and ultraviolet-visible, Fourier transform infrared, and Raman spectroscopy provide significant information about the reduction of oxygen functionalities on GO and the introduction of new functionalities in GO-ODA and GO-ANS. The effects of particle functionalization for the improved control of particle adhesion to the tribocontact have been studied. Wettability and thermal stability were determined using the water contact angle, and atomic force microscopy and differential scanning calorimetry (DSC) were used to characterize particle adhesion to the tribocontact. The tribological performances of the particles have been investigated using macro- and micro-tribometry using pin/ball-on-disc contact geometries. The influence of particle functionalization on the contact pressure and sliding velocity was also studied under rotating and reciprocating tribo-contact in ambient conditions. With an increase in the contact pressure, the functionalized particles are pushed down into the contact, and they adhere to the substrate to form a continuous film that eventually reduces friction. Amphoteric GO-ANS provides the lowest and most steady coefficient of friction (COF) under all tested conditions along with low wear depth and minimal plastic deformation. This is because particles with superior wetting and thermal properties can have better adherence to and stability on the surface. GO-ANS has a superior ability to adhere on the track to form a thicker and more continuous film at the interface, which is investigated by field emission scanning electron microscopy, energy dispersive spectroscopy, and Raman analysis.

Keywords: solid lubricants; nanoparticles; carbon; graphite; sliding friction and wear; adhesion; electron microscopy

1 Introduction

Ultra-precision mechanical assemblies like nano-electro-mechanical systems (NEMS) and micro-electro-mechanical systems (MEMS) involve micro-dynamical parts that have performances that are highly controlled by tribology [1–3]. Among the key failure mechanisms

of major machine parts, friction and wear have been the leading problem when any contacting interface rolls, slides, oscillates, or rotates over another. In the field of applied tribology, it is both challenging and necessary to control the friction and wear of mechanical contacts to efficiently conserve energy and maintain environmental cleanliness [4, 5]. Therefore,

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lubrication is a simple and effective way to overcome frictional problems while conserving energy and maintaining the durability of mechanical systems [6, 7]. For this purpose, liquid lubricants or lubricating additives are often used at the interface. However, conventional lubricating technologies are restricted owing to the viscous effects on micro-systems and limitations in extreme operating conditions such as at high or low temperatures and pressures, in reactive environments, and under radiation [8–12].

Over the years, many researchers have used various organic and inorganic nanoparticles to avoid actual surface contact and to effectively control the frictional behavior of mechanical contacting interfaces [13–21]. Solid lubricants are employed to dictate tribological performance in terms of friction, wear, and endurance life where liquid lubricants are difficult to use or in extreme operating conditions. Lower shear strength, strong substrate adherence, and structural and thermal stability of the particles are crucial factors to achieve effective solid film lubrication. Recently, it was reported that when ultrathin MoS_2 sheets are used as additives in the base oil, the ultrathin sheets can easily enter the contact area between the contacting asperities owing to their good oil-solubility and ultra-low thickness. These nanosheets can adsorb on the contact surface and act as a solid lubricant film to lower friction [22, 23]. Layered materials such as graphite, molybdenum disulfide (MoS_2), boron nitride (BN), tungsten disulfide (WS_2), and magnesium silicate ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$, talc) are used both as solid lubricants and as fillers for surface coatings in solid lubricating composites [24–27]. The low friction of both graphite and metal dichalcogenides is usually caused by interplanar mechanical weaknesses, intrinsic to their crystal structures. The weak inter-lamellar bonding in these materials facilitates the shearing when the direction of sliding is parallel to the planes of the material and it is responsible for the lubricative properties of these materials.

The lubricating application of graphene as an additive in oil has been studied over the years and the lubricity of these materials is accounted to the formation of an ordered tribofilm at the contact interface [28, 29]. Recently, graphene has attracted significant attention owing to its excellent self-lubricating

performances as a solid lubricant [30]. The tribology of graphene materials has significant advantages over graphite due to its strong chemical inertness in humid environments, novel physico-chemical properties, and strong mechanical properties [31]. In addition, the solid lubricating particles should also possess additional properties such as higher thermal stability, high load bearing ability, and larger specific surface area for better lubricating potential where the graphene materials perfectly fit in. The beneficial advantages of graphene materials have also been explored for wear-resistant and low-friction coatings on the macro/micro-scale sliding/rotating tribocontacts [32, 33]. Graphene layers are being explored as promising solid lubricants in various environmental conditions [30, 34] and as ideal solid lubricants to reduce nanoscale friction and wear [35]. Filleter et al. [36] determined that graphene films successfully deposited on SiC surfaces and epitaxially grown coatings were found to reduce friction and wear more significantly than graphite coatings. Berman et al. [37] reported that chemical vapor deposition grown graphene could be deposited on 440C steel and the coating was found to have a comparatively lower coefficient of friction (COF, about 0.2) with 40 times longer wear life in a H_2 gas environment rather than in a N_2 environment. Sumant et al. [34] investigated the friction and wear properties of chemically exfoliated graphene on 440C steel pairs under N_2 atmosphere. They reported that the COF and wear rate decreased drastically with the addition of a few layers of graphene. Most studies address the friction and wear reduction behavior at low contact pressures rather than at high contact pressures on steel–steel interfaces. Tribological failure in many cases may be attributed to the poor adhesion of graphene on the steel substrate due to the absence of surface functional groups to impart better solid film lubrication [38].

The adhesion of solid lubricant onto solid substrates is one of the deciding factors to achieve the desired durability and efficiency of lubrication [33]. Recently, the reduction as well as surface functionalization of graphene oxide (GO) simultaneously using variable organic and inorganic substances have attracted considerable attention for variable applications. GO is a precursor required to modify graphene to possess

reactive hydrophilic functional groups such as alcohols, carbonyls, and epoxides [39]. The presence of nucleophilic acceptor reactive functional groups has led to the surface modification of GO and the tuning of the adhesive properties to assist the lubrication process [38]. Lee et al. [40] reported that the improvement in frictional response observed for oxidized graphene during micro-frictional atomic force microscopy studies is due to the characteristics of the sp^2 rich subdomains. Alazemi et al. [41] demonstrated that graphene-ZnO composites have excellent friction and wear reduction properties for solid film lubrication owing to an increase in the adhesion of the coating. Recently, Saravanan et al. [42] prepared multilayer polyethyleneimine/graphene coatings for macroscale superlubricity in different gas environments via layer-by-layer deposition techniques. They reported that multilayer GO/polymer composite matrix has excellent adhesion properties via electrostatic attraction, and they provide better friction and wear reduction in N_2 gas environments. However, more studies are required to understand the mechanism of graphene-based particles that facilitates superior solid film lubrication with improved tribological factors.

In our present tribochemical study, our focus was on using surface modified graphene as solid lubricants. We attempt here to chemically alter graphite particles to GO in order to introduce dangling oxygen functional bonds. Further, we functionalize GO with organic amine functionalities (octadecyl amine (ODA) and 6-amino-4-hydroxy-2-naphthalene sulfonic acid (ANS)) to alter the thermal and structural stability to tune the lubrication needs of the contact assemblies. We report here how the chemical functionalization on GO sheets can control the wetting behavior of the functionalized particles that controls their adhesion to the contacting steel surfaces for the reduction of macro to micro scale friction and wear in a variable pressure regime. Then, we address this issue of adhesion assisted lubrication mechanism by examining the microstructural and spectroscopic properties of the functionalized particles and further characterize the particle tribofilms on the steel contacts and relate with the wetting behavior of the particles and their ability to form a transfer film under traction.

2 Experimental section

2.1 Materials

Natural graphite flakes (100 mesh, Sigma Aldrich), potassium permanganate (AR grade, Merck), 98% sulfuric acid (AR grade, Merck), sodium nitrate (ACS reagent, Sigma Aldrich), 37% hydrochloric acid (AR grade, Merck), and 30% hydrogen peroxide (AR grade, Merck) were purchased and used for the chemical synthesis of GO as received. 99% hydrazine monohydrate (AR grade, Merck) was utilized as a reducing agent. Octadecyl amine (97%, Sigma Aldrich) and 6-amino-4-hydroxy-2-naphthalene sulfonic acid (Technical grade, Sigma Aldrich) were purchased and used as the simultaneous reducing and surface modifying agent without further purification. Commercially available hardened 440C stainless steel (0.15% carbon, 1% manganese, 0.04% phosphorus, 0.03% sulfur, 1% silicon, 11.5%–13.5% chromium, 50 HRC) was used as the substrate material for tribological investigation.

2.2 Preparation of chemically modified nano solid lubricant particles

Herein, a modified Hummer's method is employed for the preparation of GO from graphite flakes as reported in our previous study [43]. GO was used as the precursor to create the modified reduced graphene (r-GO) for solid lubrication purpose. The modification of GO with long chain octadecyl amine was achieved by a simultaneous functionalization and chemical reduction process to create a hydrophobic counterpart. Typically, 400 mg of GO was dispersed in 200 mL of deionized (DI) water (Merck, resistivity $\sim 18.2 \text{ M}\Omega\cdot\text{cm}$) and exfoliation was obtained via ultra-sonication in a bath for 30 min in a 500 mL round bottom flask. Then, the unexfoliated GO was removed by centrifugation for 15 min at 3,500 rpm. Further, 0.6 g of ODA was dissolved in 100 mL ethanol and mixed with a stable GO dispersion. This mixture was refluxed with continuous stirring for 24 h at 120°C followed by the addition of 3 mL hydrazine monohydride and an additional 6 h refluxing process. The resultant solution was filtered using millipore membrane filter paper (cellulose acetate, average pore size $0.22 \mu\text{m}$) and was

repeatedly washed with ethanol/DI water to remove physically absorbed and unreacted ODA molecules or any other contaminants. Finally, the black hydrophobic ODA-functionalized GO powder (GO-ODA) was collected and dried in a vacuum oven for 2 days at 70 °C. The wettability of the lubricating particles was a key parameter to assess solid film lubrication. To compare with hydrophobic GO-ODA particles, we have further modified GO particles with ANS to prepare hydrophilic GO-ANS. In brief, 300 mL water dispersion of GO (1 mg/mL) was poured into a 1,000 mL round bottom flask. Then, 750 mg of ANS was dissolved in 250 mL of DI water in a 500 mL beaker. The ANS solution was added to the GO dispersion and refluxed at 110 °C in a pre-heated oil bath for 24 h. The refluxing procedure was continued for another 12 h after the addition of 0.3 mL hydrazine monohydrate. Then the reaction mixture was filtered through cellulose acetate membrane (pore size 0.22 μm) filter paper and was washed with DI water several times to remove unreacted reagents. Then the resulting functionalized GO (GO-ANS) was dried in a vacuum oven at 70 °C for 2 days for physico-chemical and tribological studies.

2.3 Structural and chemical characterization techniques

The UV-Vis absorption spectra of the GO and its modified parts were acquired using a SEC2000 ALS spectrometer (Japan) where the path length of the quartz cuvette was 1 cm. A Perkin–Elmer Spectrum 100 spectrometer (USA) was used for the acquisition of the FT-IR spectra of all the modified graphitic particles in the form of as-prepared KBr pellets. The structural characteristics and crystallinity of the modified graphitic powders were analyzed by the powder X-ray diffraction method using an X-ray diffractometer (Philips Panalytical X Pert Pro, UK) at 45 kV and 40 mA using Cu-K α radiation ($\lambda = 0.1542$ nm). The diffraction peaks in the form of the 2θ angle were measured between 10° and 60°. The Raman spectral analyses of GO, GO-ODA, and GO-ANS were performed at room temperature using a confocal AFM–Raman spectrometer (WITec, alpha 300R, Germany) that was calibrated with a Si line using a lower wavelength of 520 cm^{-1} . A Nd:YAG laser source was used, which was capable of supplying 75 mW of power

at a 532 nm excitation wavelength. AFM force curve measurements are performed using a Si tip in contact mode. The particle size distribution of the GO particles was carried out in aqueous/oil suspension through a dynamic light scattering using a Zetasizer nano ZS nanoparticle size analyzer (Malvern Instruments, UK) with 4 mW He-Ne laser source. A 0.1 wt% (w/v) particle suspension was used in a 1 cm diameter DLS cell and the data was collected using an avalanche photodiode detector. The heating rate and thermal stability of the particles were characterized using differential scanning calorimetry (DSC) using a calorimeter (DSC 204 F1, Phoenix®, NETZSCH, Germany). The wettability of the particles was characterized by water contact angle measurements using an OCA 15pro commercial goniometer (Data physics, Germany). The water contact angle was measured by the sessile drop method for the motion of the three-phase contact line between water and particle surface. A JEM-3010 Transmission Electron Microscope (Jeol, Japan) was used with an accelerating voltage of 200 keV for the morphological analysis of the particles. For this analysis, the ethanolic dispersed particles were drop cast onto a copper TEM grid.

2.4 Tribological characterization

Tribological investigations were carried out with a macrotribometer (DUCOM, Bangalore, India) and a microtribometer (UMT-2, Bruker, USA). In order to examine the effects of contact pressure on frictional behavior, the macrotribological tests were performed using a pin/ball-on-disc configuration under two different pressure regimes. Before tribological tests, the disc samples (RMS roughness ~ 400 nm) were polished with emery paper (using grit sizes of 400, 800, 1,200, and 2,000) followed by cloth polishing with a diamond paste of grades 1–3 μm , on a double-disc polishing machine (BAINPOL, Chennai Metco Pvt. Limited, India). The polished discs were cleaned with ethanol/acetone prior to the tribological experiments. For pin-loading macrotribological experiments, a 4 mm diameter steel pin was loaded into the pin holder against a rotating disc with a 0.4 m/s surface speed. A 10 mm diameter ball (chromo steel, RMS roughness ~ 5 nm) was used for ball-on-disc tests. Before all pin loading tests, the pins were run against the polished

disc in an unlubricated condition with a 5 N load for 3 h to achieve maximum pin-on-disc contact. The modified solid lubricant particles were suspended in hexane and were spin coated onto the disc surface for the pin/ball-on-disc experiments. The pin/ball-on-disc experiments were performed on the coated disc at ambient conditions.

The microtribological tests were acquired in a Universal Mechanical Tester (UMT-2, Bruker), containing a 2-axis friction/load sensor (Range ~ 0.05–5 N, Resolution ~ 0.25 mN). Microtribological ball loading experiments were carried out at a 5 N load (mean Hertzian pressure, $P_m \sim 1.1$ GPa) using a 6 mm diameter ball (RMS roughness ~ 5 nm) in two different sliding speed conditions (low speed at 0.5 mm/s and high speed at 5 mm/s). All measurements were performed using a reciprocating mode in ambient conditions with 60 minutes of sliding time for both speed conditions. Normal and friction forces were determined using a force sensor whereas the wear profile of the coated sample specimens was measured using the z-axis displacement.

To explore the status of the particles in the slid track of the tribological tests, the worn surfaces were subjected to further microscopic and spectroscopic investigations. Optical images of the slid tracks were obtained using a Nikon optical microscope (Micropublisher 3.3 RTV, JAPAN). The microscopic features of the tribotacks were obtained using a field emission scanning electron microscope (FE-SEM, sigma HD, Carl Zeiss, Germany). Spectroscopic analyses of the worn tracks on the disc were investigated by Raman spectroscopy and electron dispersive spectroscopy (EDS) with Sigma (Zeiss, Germany) scanning electron microscope equipped with an X Flash Detector 4010 (Bruker, USA).

3 Results and discussion

The UV-Vis absorption spectra of the GO and GO-ANS in water and GO-ODA in chloroform are shown in Fig. 1(a). The GO particles clearly showed two absorption peaks at 232 and 310 nm. The peak at 232 nm was associated with a $\pi \rightarrow \pi^*$ transition along with a shoulder peak at 310 nm for the $n \rightarrow \pi^*$ transition due to the presence of the oxygen functionality on the GO. However, with an ODA functionalization,

Fig. 1 (a) UV-Vis absorption spectra of GO, GO-ANS in aqueous and GO-ODA in chloroform medium. (b) FT-IR transmittance spectra of GO, GO-ODA and GO-ANS.

the $\pi \rightarrow \pi^*$ peak red shifted towards the restoration of the $\pi \rightarrow \pi^*$ conjugation in the GO-ODA sample. However, the $n \rightarrow \pi^*$ transition at 310 nm completely disappeared, suggesting that the oxygen-containing groups were reduced, leading to extended graphitization [43]. Similarly, the $\pi \rightarrow \pi^*$ peaks of the GO-ANS appeared at 260 nm with the absence of characteristics of a $n \rightarrow \pi^*$ transition.

The FT-IR transmittance spectra of the functionalized particles are shown in Fig. 1(b). The GO particles showed a stretching and deformation peak characteristic of $-\text{OH}$ functional groups at $3,410\text{ cm}^{-1}$. The carboxyl functionalities ($-\text{COOH}$) of GO appeared at $1,720\text{ cm}^{-1}$. The peak positions at $1,627$, $1,368$, $1,235$, and $1,092\text{ cm}^{-1}$ correspond to the $\text{C}=\text{C}$ skeletal vibrational peak, the epoxy groups, and the alkoxy groups of GO, respectively [44]. For the functionalized GO (GO-ODA and GO-ANS), the carboxyl peak at $1,720\text{ cm}^{-1}$ completely disappeared along with a reduction in epoxy/hydroxyl peak intensity, suggesting that the reduction of the oxygen containing groups occurs during the functionalization process. GO-ODA and GO-ANS (Fig. 1(b)) demonstrated two new peaks at $2,920\text{ cm}^{-1}$ and $2,850\text{ cm}^{-1}$, which were described as the $-\text{C}-\text{H}$ anti-symmetric and symmetric stretching modes of the methylene group along with the $-\text{C}-\text{H}$ bending vibrational signature at 721 cm^{-1} [45]. The GO-ODA samples showed comparatively higher $-\text{C}-\text{H}$ intensity due to the grafting of long ODA chains. Another characteristic new peak at $1,564\text{ cm}^{-1}$ ($-\text{CONH}$ group) was recorded due to the reaction between the amine groups of the ODA/ANS and the carbonyl/epoxide functionality on the GO. In the case of GO-ANS, the additional new peaks at $1,190\text{ cm}^{-1}$ and $1,110\text{ cm}^{-1}$ were recorded which indicated the presence of sulfonate ($-\text{SO}_3^-$) groups on the GO-ANS samples.

Raman analysis has been an effective tool to determine the degree of structural defects and long-range order in the graphitic particles. The Raman spectral analyses of GO, GO-ODA, and GO-ANS are shown in Fig. 2(a). There are two main peaks, namely the D band and the G band, where the degree of graphitization (the existence of the sp^2 character of the graphite lattice) is denoted by the G band and the measurement of the graphitic defects appeared in the graphitic framework (A_{1g} symmetry is associated with the breathing modes of K-point photons) which is described by the D band peak. The peak of the G band of the GO was located at $1,598\text{ cm}^{-1}$, which was much broader and shifted compared to a natural graphite peak ($1,581\text{ cm}^{-1}$). This shift occurs because after oxidation, the resonance of isolated double bonds occurs at higher frequencies than the graphitic G band peak due to the loss of the sp^2 network on graphitic frame [46]. The D band peak appeared for GO at $1,348\text{ cm}^{-1}$, which was more red-shifted than that of pristine graphite, suggesting that the graphitic sp^2 framework was somewhat distorted upon oxidation. After the functionalization of GO with ODA, the G band peak shifted to $1,587\text{ cm}^{-1}$, similar to unmodified graphene ($1,584\text{ cm}^{-1}$). This shift suggests that the graphitic sp^2 character reappeared upon functionalization and reduction with ODA. For the functionalized GO-ANS, the G band peak also shifted to $1,585\text{ cm}^{-1}$ towards $1,582\text{ cm}^{-1}$ peak of graphite, showing a larger degree of sp^2 domain recovery. The characteristic intensity ratios (I_D/I_G) of both the GO-ODA and the GO-ANS were found to decrease as compared to GO. The decrease in the intensity ratio (I_D/I_G) of the Raman signal confirmed a reduction in the degree of disorderiness and the presence of the sp^2 character on the graphitic skeleton and also suggests that an effective

Fig. 2 (a) Raman spectra of GO, GO-ODA and GO-ANS. (b) Particle size measurements of graphite, GO, GO-ODA and GO-ANS in the oil/water suspension mixed using an ultrasonic probe.

functionalization and reduction of GO occurred using ODA and ANS.

In typical tribological applications, the particle size of the solid lubricating materials and their adhesive bonding to the metallic substrate play important roles. Solid particles need to migrate and stay in the asperity zone during loading and shearing to form an antifriction transfer film. Therefore, controlling the particle size is a great challenge when trying to understand lubrication mechanisms [16]. Figure 2(b) showed the average particle size of graphite, GO, GO-ODA, and GO-ANS in water/paraffin oil measured with dynamic light scattering techniques. The dispersion stability of hydrophilic GO was very poor compared to the hydrophobic graphite in oil and showed a higher average particle size of $\sim 580\text{ nm}$ whereas, in water, the dispersion stability showed an opposite behavior due to the presence of oxygen functionality on the GO. The introduction of hydrophobicity post functionalization and reduction with ODA was due to the insertion of long hydrocarbon chains which facilitated its dispersibility in a nonpolar solvent. The GO-ODA showed a lower average particle size (280 nm) in the non-polar oil compared to GO. However, due to its hydrophobic nature, its dispersibility in water is very poor. GO-ANS behaved in a very different manner in both of the dispersion medium. The presence of the amphoteric ANS chains on the GO facilitated its bipolar character and dispersion in both polar and non-polar solvents. Figure 2(b) shows that the average particle size of GO-ANS was significantly lower compared to GO in both the oil and water medium. The formation of layers might be responsible for the lower average diameter of the GO-ANS particles compared to the GO particles in water during the reduction and functionalization process. The layer formation in functionalized GO-ANS is confirmed by morphological analysis which will be discussed later.

The wetting properties and the effect of functionalization were examined through water contact angle measurements on individual particle pellets, which are shown in Fig. 3. Pristine graphite is hydrophobic in nature with a water contact angle of $\sim 90^\circ$. However, the wettability and surface energy of the particle can be altered by controlled surface modification [47]. GO largely contains hydroxyl, epoxide, and

Fig. 3 Water contact angle measurements on (a) GO, (b) GO-ODA, and (c) GO-ANS pallet.

carboxylic groups, therefore making it hydrophilic in nature and which is confirmed by its water contact angle of 50.2° . Whereas, after functionalization with ODA, the presence of long hydrocarbon chains makes the GO-ODA hydrophobic in nature. The contact angle recorded on the GO-ODA surface increases to 110.1° , which is similar to a self-assembled monolayer (SAM) of C18 silane on Si or Al [48]. However, the functionalization with amphiphilic ANS, which contains polar hydroxyl and sulfonate group, leads to an amphoteric material with a water contact angle of 66.1° .

The GO and modified particles have been shown to undergo structural changes, which were examined using XRD analysis and are shown in Fig. 4(a). GO showed an intense diffraction peak (d002) with corresponding higher d-spacing (0.78 nm) at $2\theta = 11.5^\circ$. The characteristic (200) plane is responsible for the interference effect of the interlayers. The higher d-spacing (interlayer distance) of the GO sheets is indicative of the extendable turbostratic interlayer stacking of nanographite with hydrophilic oxygen functionality [49]. Another low-intensity diffraction peak at $2\theta = 43^\circ$ is attributed to the (100) plane. This peak explains the turbostratic disorder in the interlayer structure of the graphitic plane that is also well explained by the Raman spectra in Fig. 2(i). However, the addition of ODA and ANS chains made a distinct structural change in the graphitic plane. The (002) peak of the GO is shifted to 21° for the GO-ODA with a lower interlayer spacing of 0.41 nm, which is analogous to pristine graphite (interlayer distance 0.34 nm) [50, 29]. The (100) peak is observed in the respective position with lower intensity. This peak shift indicated the removal of an intercalated oxygen group from the disordered sheets during the modification with ODA. Similarly GO-ANS showed a broad diffraction peak (002) at 22.5° with an interlayer

spacing around 0.37 nm, which indicated a successful reduction as well as a higher degree of sheet formation.

The thermal stability of the lubricated particles is an important parameter for solid film lubrication. The DSC analysis of GO and its modified parts (GO-ODA and GO-ANS) are shown in the Fig. 4(b). Characteristic DSC analyses were carried out in the temperature ranges from 20 to 600°C . For GO, two different peaks were observed, one endothermic peak near 80°C due to the absorbed water molecules in GO, which need additional heat to escape from the bulk. Another strong exothermic peak was observed near 200°C due to the decomposition of all the oxygen functionalities in GO. This exothermic peak is due to the decomposition of the attached oxygen functionalities (such as hydroxyl, epoxy and carboxyl) as CO_2 gas and H_2O [51, 52]. However, after functionalization of GO by ODA, three different peaks were observed. An endothermic peak at 40°C appeared due to the presence of adsorbed water molecules on the hydrophobic GO-ODA. A low intensity exothermic peak near 180°C was observed due to the degradation of the remaining oxygen-containing groups after the functionalization process by ODA. Another broad endothermic peak was observed $\sim 430^\circ\text{C}$ which may be due to the decomposition of long alkyl chains from the GO surface. For GO-ANS, two very weak peaks at 40°C and 80°C were observed. The first peak is due to the evaporation of the adsorbed water molecules and the second peak is due to the release of absorbed water from the amphiphilic GO-ANS. The last peak is attributed to the removal of the remaining oxygen-containing groups after functionalization by ANS. A few very weak peaks were also observed $\sim 200^\circ\text{C}$ and $\sim 470^\circ\text{C}$ which may be due to the decomposition of the remaining oxygen functionalities and attached ANS molecules, respectively. This study suggests that

Fig. 4 (a) XRD patterns and (b) DSC curves of GO, GO-ODA and GO-ANS.

the thermal stability of the GO-ANS and the GO-ODA are much better than GO.

The morphological features of the functionalized graphitic particles were examined using TEM micrographs. TEM micrographs of GO revealed an extended thin film with a wrinkled edge surface [53], as shown in the Fig. 5(a). The exfoliation of the individual GO sheets and its wrinkled structure is responsible for the prevention of restacking and the high surface area of the structure. However, the covalent grafting of the ODA on the GO surface is attributed to the assembly of several folded layers with a wrinkled edge, in Fig. 5(b). This structure might be caused by the entanglement of long ODA chains on the GO sheets and might be the reason for poor wetting and better dispersion behavior of the GO-ODA (Figs. 2(ii) and 3) in oil. The GO-ANS samples clearly exhibited (Fig. 5(c)) nanosheets with wrinkled regions and somewhat rough surfaces. The multilayer formation improved the particle diameter over GO (Fig. 2(ii)) with the presence of small hydrophilic ANS to enhance surface corrugation.

3.1 Tribological investigations

The tribological tests were performed with modified graphitic particles at a steel-steel interface using a macro/micro tribometric pin/ball-on-disc arrangement under ambient condition. For the solid film lubrication studies, the individual solid particles (graphite, GO, GO-ODA and GO-ANS) were dispersed in hexane using ultrasonication and were spin coated on the disc surface. All the pin/ball-on-disc tests were conducted for 60 minutes. To tune the coefficient of friction and wear effectively in the tribo-contact zone, access of the particles to the contact zone, adhesion and load bearing ability of the lubricated particles are essential

requirements. To address this issue, we started here with the oxidation process of the graphitic skeleton and further introduced various organic moieties (ODA and ANS chains) on the graphitic basal plane to alter their wetting behavior, which may directly affect their adhesion to the substrate and tune the lubrication behavior as required by the application. Here we focus on how the surface-active solid lubricant additives control the coefficient of friction and the wear with varying tribological parameters (contact pressure, sliding speed).

Figure 6 showed the variation in the coefficient of friction (COF) with sliding time in the pin loading (mean Hertzian pressure, $P_m \sim 0.9$ MPa) and ball loading ($P_m \sim 1.4$ GPa) macrotribological tests at 30 N normal load with 0.4 m/s sliding speed for functionalized graphitic particles under ambient conditions. In order to better compare the lubricity of the prepared functionalized particles, we first examine the frictional behavior of graphite, a well-known solid lubricant and the precursor to the functionalized particles, in dry conditions under pin/ball loading contact (Fig. 6). The COF of graphite increases gradually with sliding time and reaches a value of ~ 0.18 – 0.2 for pin loading at 30 N load (Fig. 6(a)). However, with an increase in contact pressure (ball loading experiment), the same particle provided a much lower COF of ~ 0.12 – 0.14 (Fig. 6(b)). For the solid particles to offer an effective lubrication they need to remain and adhere to the substrate in the tribo-contact zone [15, 16, 27]. Therefore, durability at the contact point is one of the key lubrication criteria for a good solid lubricant. However, the main problems with using graphite as a solid lubricant are its low dispersibility, poor thermal stability, poor adhesion, and shorter service life in the contact zone. However, after functionalization of the graphitic

Fig. 5 HRTEM micrograph of (a) GO, (b) GO-ODA, and (c) GO-ANS.

Fig. 6 Variation in friction coefficient with time data for the functionalized lubricant particles in the ambient from the (a) pin loading ($P_m = 0.9$ MPa) and (b) ball loading ($P_m = 1.4$ GPa) tribometric studies at normal load of 30 N with sliding speed of 0.4 m/s.

moieties with polar oxygen functionalities and further with organic amine functionalities, the resulting particles work in a controlled manner as per their functional conditions. We attempt to identify the effects of contact pressure on particle adherence and solid film tribo-contact of the various particles to realize their frictional behavior.

From the time dependent friction map of the pin and ball loading tests, it is found that the particles were better able to control the friction and provide a lower COF in high pressure ball loading tests than the pin loading tests. Under increased pressure, the particles are pushed down into the contact and adhere to the substrate to form a continuous film which eventually reduces the friction. At high pressure, the interlayer slip between the particles helps to form a thick film, as has been reported earlier [16]. The frictional trace of the functionalized particles was found to be similar to graphite for low-pressure conditions except for the GO-ODA samples, which showed a higher friction (>0.2). The anomalous behavior of GO-ODA may be attributed to poor adherence to the substrate due to its hydrophobic nature. Moreover, the friction of the GO was found to be linear till sliding time $\sim 2,600$ s under the pin loading condition. After that, the COF increased rapidly with abnormal fluctuations until the end of the experiment, which may be due to its poor thermal stability as shown in Fig. 4(b).

Under high-pressure ball loading conditions, the solid particles have better friction reduction efficiencies than under low-pressure pin loading conditions. The COF of the GO was found to be minimal (0.05) until a sliding time $\sim 1,800$ s after which it gradually increased

to a higher level (~ 0.2). This may be due to the partial removal or poor stability of the surface film under high pressure with increasing sliding time. GO-ODA displayed the highest COF among the particles with an abnormal increase at higher sliding times. Similar to pin loading condition tests, the particle adherence to the contact is poor due to the poor adhesion of the hydrophobic GO-ODA, and the advantages were completely lost at higher pressure and increased sliding time. However, GO-ANS showed completely different frictional behavior with respect to the contact pressure. With increasing pressure, hydrophilic GO-ANS provided the lowest and most steady COF (0.06) among the lubricated particles as a function of time.

The above tribological results suggest that the wettability and surface properties of the functionalized particles are deciding parameters which dictate solid film lubrication. Graphite works well as a solid lubricant due to its layer structure [26], which easily smeared under traction in the contact zone. Owing to the inter-lamellar structure of the graphite, the formation of a smooth transfer film at the contact interface is facilitated and the transfer film is able to withstand the load under traction to provide a steady COF (Figs. 6(a) and 6(b)). To survive solid film lubrication, the adhesion of the nanoparticles to the contact region between the asperities of the mating surfaces is very much crucial. The inter-lamellar structure of the graphite is broken upon oxidation to form GO. Therefore, the penetration of the GO particles between the asperity contact points is difficult under pin loading (low-pressure) condition. For this reason, the initial COF of GO is comparatively higher than that of graphite and, with time, almost becomes comparable with graphite as the tribofilm builds up. In the later stages of the experiments, the COF is very high as the film wears out during contact due to its poor thermal stability. With increasing pressure, the trapped GO particles are pushed down in the contact and adhere to the substrate more efficiently due to its polar character to form a continuous film which eventually reduces the friction to a lower level (0.05). However, after a certain amount of time, the lack of sufficient adhesion and low thermal stability (Fig. 4(b)) might force the film to break down the tribotrack and the COF value increases to higher level (~ 0.2). In case

of the GO-ODA, the graphitic layer structure was somewhat damaged by the introduction of long alkyl chains during chemical modification and due to removal of oxygen functionalities, the thermal stability improved significantly on GO-ODA sheets (Fig. 4(b)). However, due to its hydrophobic nature, the adhesion of the GO-ODA to the substrate is very poor and it is unable to persist at the sliding interface and is unable to form an effective anti-friction transfer film. With a change in the wetting behavior of the particles (Fig. 3(b)), the adhesion of these particles was also varied, which could reflect in their ability to form a particle film in the contact interface.

AFM force measurements can provide important information about the adhesion between the particle surface and the AFM tip. Figure 7 shows the approach–retraction force distance curves on the lubricant particles taken with a hydrophilic Si AFM tip. The approach part of the curve provides information about the interaction between the tip and the surface and the retraction part of the curve provides information about the adhesion force. Under ambient conditions, the particle surfaces are likely to be concealed with a thin capillary of an adsorbed water layer, depending on their wetting behavior. Therefore, the hydrophilic particles may absorb more water and may result in large tip–sample adhesion values compared to hydrophobic particles. Compared to pristine graphite particles (CA $\sim 90^\circ$), the polar GO particles (CA $\sim 50.2^\circ$) show much higher pull off adhesion forces due to the presence of a prominent adsorbed water layer on the surface. After functionalization of the hydrophilic GO particles into the hydrophobic GO-ODA (CA $\sim 110.1^\circ$), the adhesion force was reduced significantly. However, in the tests of the amphoteric GO-ANS, the pull off force between the tip and GO-ANS is, due to their polar nature, significantly higher than that of the GO-ODA particles and almost comparable with the GO particles. This can be easily described by the Young-Dupre equation [47]. As per the Young-Dupre equation, $\gamma_l (1 + \cos\theta) = W_{sl}$, where γ_l is the surface tension of the water, θ is the contact angle and W_{sl} is the work of adhesion at the solid–liquid interface. This suggests as θ becomes smaller (hydrophilic), there will be an increased adhesion of the particles with the substrates. This could lead to the formation of a stable continuous film at the interface and, as per

Fig. 7 Approach–retraction force–distance curves measured on graphite, GO, GO-ODA and GO-ANS particles.

their thermal stability, the particles stay in the contact to bear the load and provide lubrication. The hydrophilic group containing ANS chains on the GO made GO-ANS amphoteric in nature (Fig. 3(c)) which may facilitate better adherence to the steel surface. Under higher contact pressures, the hydrophilic GO-ANS particles have a superior ability to smear on the track to form a thicker and more continuous film at the interface, which eventually reduces the friction to a lower level (Fig. 6). The usability of the ANS-functionalized particles is also aided by an enhanced thermal stability of the resulting functionalized particles which were found to be beneficial not only for better lubricity but also improving the longevity of the interfacial tribofilm.

In order to access the above proposition, we compared the optical images of the worn tribotacks acquired from the pin and ball loading tests in the macrotribological tests of graphite generated in ambient conditions (Figs. 8(a) and 8(b)). Figure 8(a) shows the presence of a thin irregular particle film on the disc surface for the pin loading tests. However, for the ball loading trials, the film formed on the worn track was found to be thick and continuous (Fig. 8(b)). As we discussed earlier, under higher contact pressures particles will be pushed down into the contact region and smear on the track to form a continuous film which may reduce the friction to a lower level (Fig. 6). Further, we compared the optical images of the tribotacks from the ball loading POD tests of the GO-ODA and the GO-ANS with variable wetting behavior. Figure 8(c) showed the presence of a thin smeared film and a few broken and agglomerated particles on the worn track with large track width (850 μm) when the GO-ODA was used at

Fig. 8 Optical images of the POD tribometer tracks of graphite generated with (a) pin and (b) ball loading tests and tribometer tracks generated with ball loading tests for (c) GO-ODA and (d) GO-ANS at 30 N normal load in ambient condition.

the interface. However, with hydrophilic GO-ANS, the lubrication behavior seems to differ from the behavior of the hydrophobic GO-ODA. A well-adhered thick and continuous transfer film, along with large number of particles, was found on the track (Fig. 8(d)). The worn track width for the GO-ANS test was considerably smaller ($\sim 510 \mu\text{m}$) compared to the GO-ODA test. This indicates better adhesion of the ANS to the steel-steel tribocontact than hydrophobic GO-ODA, resulting in the formation of a thick stable anti-frictional transfer film, which eventually reduces the COF and worn track width (Figs. 6 and 8(d)).

Further, the tribological behavior of the prepared particles were investigated in a ball on disc microtribometer. The experiments were conducted under a 5 N load ($P_m \sim 1.1 \text{ GPa}$) with a similar contact pressure to that used in the macrotribometric ball loading tests, at two different sliding speeds (low speed at 0.5 mm/s and high speed at 5 mm/s) in ambient condition in order to explore the effects of sliding speed on dry film lubrication. Higher sliding speed is normally associated with higher contact temperature, which plays a major role in deciding the lubricating ability of the solid lubricant particles. Under these conditions the thermal stability of the particles is expected to play an important role. The effect of sliding speed on the frictional behavior of the particles was more evident as the frictional map (Figs. 9(a) and 9(b)) of the functionalized particles at different sliding speeds was found to be different. The results from

Fig. 9 Variation in friction coefficient with time data for graphite, GO, GO-ODA and GO-ANS in the ambient from the (a) low speed (0.5 mm/s), (b) high speed (5 mm/s) and corresponding wear depth with sliding time data from the (c) low speed, (d) high speed microtribometric ball loading studies at normal load of 5 N ($P_m = 1.1 \text{ GPa}$) with sliding stroke length of 4 mm.

high pressure macrotribometric data was found to be similar to the macrotribometric data observed at a lower sliding speed. With an increase in sliding speed, a diverse behavior is observed depending on the adherence of the particles and the life of the tribofilm at contact. Graphite showed a different frictional trend with respect to the varied speeds (Figs. 9(a) and 9(b)). At low sliding speeds (LS), graphite showed low (0.08–0.1) and steady COF and the values are almost similar to what we observed in the ball loading macro tests. However, with high sliding speeds (HS), the value of the COF was initially similar to the low speed results, but rapidly increased in value to reach the steady state metal-on-metal value (Fig. 9(b)). The initial COF of GO was found to be much higher and may be due to bigger GO being particles unable to infiltrate into the contact zone. With increasing time, the frictional behavior of the GO was found to be linear (Fig. 9(a)) as the ruptured particles are trapped and build a stable interface film. With increased sliding speed (HS), under a more dynamic condition, larger particles are trapped more easily and under load the particles are ruptured and stick to the interface. However, after $\sim 1,800 \text{ s}$, the rapid increase of the COF value (~ 0.3) might be due to the removal of the tribofilm owing to the poor thermal stability of the GO. The hydrophobic GO-ODA showed a comparatively lower COF (0.1) initially until $\sim 1,200 \text{ s}$, afterwards

increasing substantially to ~ 0.18 for the LS condition and ~ 0.4 for the HS condition, followed by abnormal fluctuations until the end of the test (Figs. 9(a) and 9(b)). The initial low COF value of the GO-ODA tests might be due to the presence of long carbon chains attached to the GO sheet, which helps to form a load bearing barrier in the interface. However, the low adhesive GO-ODA particles are removed from the contact region with increased sliding time and speed. In contrast, GO-ANS displayed a continually lowest COF among the particles at both speed conditions (0.08 for LS and 0.1 for HS). Amphoteric ANS chains may have better wetting properties and the presence of sulfur might assist in the superior adhesion of the GO-ANS particles to the steel substrate and create a negligible COF between the particles [54].

Herein, we also correlate the frictional response with corresponding wear depth data for solid lubricated particles in both of the speed conditions. The above frictional data were found to be in an order according to their corresponding wear depth value (Figs. 9(c) and 9(d)). At LS, graphite displayed a wear depth up to $8\text{ }\mu\text{m}$ whereas with increasing speed (HS), the wear depth value increased to $15\text{ }\mu\text{m}$, which shows that the deposited particles were removed from the interface which results in a metal to metal contact at higher speeds. Hydrophilic GO particles showed comparatively low wear depth ($\sim 4\text{--}5\text{ }\mu\text{m}$) in LS tests until a sliding time $\sim 1,200\text{ s}$, after which wear linearly increased to $\sim 10\text{ }\mu\text{m}$. In the HS condition, the wear depth value increased to a maximum of $\sim 14\text{ }\mu\text{m}$. In the case of the hydrophobic GO-ODA in the LS

condition, the wear depth value started to increase rapidly after initial sliding and reached a maximum value of $\sim 11\text{ }\mu\text{m}$. This may be due to the poor adherence as discussed earlier. However, in the HS condition, wear depth was found to be similar to the LS condition and was lower than the GO due to the enhanced thermal stability of the GO-ODA and the presence of long hydrocarbon chains as a cushioning barrier between the steel-steel interface. However, the amphoteric sulfur-containing GO-ANS demonstrated the lowest wear depth ($\sim 6\text{ }\mu\text{m}$) among the particles irrespective to the sliding speed (Figs. 9(c) and 9(d)), thus showing the best tribological characteristics among all the particles.

In order to better characterize the effect of sliding speed on solid lubrication, FE-SEM analysis of wear tracks was performed. Figure 10 shows the FE-SEM images of the wear track surfaces of the dry lubricated tests with functionalized graphitic particles after sliding for 3,600 s at both sliding speed conditions (LS/HS) and a 5 N normal load. As shown in Fig. 10(a) and 10(d), the wear tracks of the GO lubricated films displayed a wear track with a width $\sim 150\text{ }\mu\text{m}$ with a non-continuous film on the track along with discrete wear particles. However, the worn track width increased significantly ($\sim 275\text{ }\mu\text{m}$) at higher sliding speeds due to the increase in plastic deformation of the particles. The increase in track width and plastic deformation indicates the removal of the particle film from the counterface at HS and is responsible for the high COF (Fig. 9(b)). The worn track surfaces of the GO-ODA tests are shown in Figs. 10(b) and 10(e), and a transfer

Fig. 10 Post microtribological FE-SEM images and corresponding worn track width of the tribometer track generated for ball loading ($P_m \sim 1.1\text{ GPa}$) on disc surface with (a) GO, (b) GO-ODA, (c) GO-ANS for LS and with (d) GO, (e) GO-ODA, (f) GO-ANS for HS ambient condition.

particle film is observed with a comparatively larger track width ($\sim 260\ \mu\text{m}$) in both the sliding conditions. This may be due to the poor adhesion and plastic deformation of the particles and as a result, the width of the worn track increased due to the poor adherence of the hydrophobic particles to the steel surface. In tests with the GO-ANS on the surface, the wear track width was reduced significantly ($\sim 110\ \mu\text{m}$ for LS and $\sim 170\ \mu\text{m}$ for HS) with a smooth and continuous particle film observed in a worn track surface at both speed conditions (Figs. 10(c) and 10(f)). This result confirms that GO-ANS particles are more efficient for solid film lubrication in ambient conditions and forms surface-active adhesive film which efficiently reduces COF and wear depth (Figs. 9(a) and 9(b)).

Further EDS spectral analyses were recorded on the worn tracks to corroborate the elemental compositions of the wear film present in the tracks, which is shown in Fig. 11. The comparable elemental study (wt%) is given in Table 1. The worn track surface for GO in LS shows preeminent carbon signature along with an oxygen peak with a nominal Fe signature (Fig. 11(a) and Table 1). However, at the HS condition, the Fe signature increases significantly indicating the removal of particle film from the rubbing tribo contact (Fig. 10(d)). However, with GO-ODA, in both the LS and HS tribotest, the elemental carbon signature is reduced compared to the GO tests, the oxygen peak vanished, and a higher Fe signature is seen in the LS condition, indicating the presence of a thin particle film. In the HS condition, the particle film is removed from the contact region due to plastic deformation of the surface inactive hydrophobic GO-ODA particles (Fig. 10(e)) resulting in a further increase in Fe signature. Conversely, the EDS spectra for GO-ANS exhibited (Fig. 11(c)) an increased carbon signature along with oxygen and sulfur peaks and a nominal Fe content in both the LS and HS condition (Table 1) indicating the existence of a thick particle film which eventually reduces COF and wear depth. Therefore, the capability of the nanoparticles to enter the contact region, the adhesion of the particle to the rubbing surfaces, the wettability, and the size of the particles are the key factors which dictate the lubricity of the materials along with tribological parameters. Herein, the sulfur-containing ANS chains in the GO-ANS (Table 1) demonstrate superior surface-active adhesive

Fig. 11 Post microtribological EDS spectra of the worn disc track generated for LS ball loading dry sliding tests with (a) GO, (b) GO-ODA, (c) GO-ANS and for HS condition with (d) GO, (e) GO-ODA, (f) GO-ANS.

Table 1 Elemental wt% from EDS analysis in tribo track surfaces from micro tribological ball loading tests for graphite, GO, GO-ODA and GO-ANS in both LS and HS ambient condition.

Element (wt%)	Graphite		GO		GO-ODA		GO-ANS	
	LS	HS	LS	HS	LS	HS	LS	HS
C	64.16	8.62	52.85	36.19	43.65	37.75	57.52	54.69
O	2.03	2.35	12.22	8.96	3.14	2.73	12.03	11.8
S							0.87	0.64
Fe	33.8	89.03	34.93	54.85	53.21	59.52	29.58	32.86

properties that can be assembled at the contact interface to form a thick protective tribofilm to impart superior lubricity.

Further, post tribological Raman spectra were carried out on the tribofilm generated during the microtribological tests using the functionalized particles to examine the nature of deposited particle film. The Raman spectral study of the worn tracks (LS and HS tracks) generated with GO, GO-ODA and GO-ANS in dry lubricated tribotests is presented in Fig. 12. Figure 12(a) showed a weak intensity Raman signal (G band peak at $1,596\ \text{cm}^{-1}$) for the particle film generated with GO at the HS condition whereas at the LS condition, a Raman signal was visible at a much higher intensity at the respective D and G band peak position. The higher intensity signal indicates the presence of a significantly thicker particle film on the wear track [15, 43]. The worn track, corresponding to the GO-ODA at LS condition, showed the characteristic

G band at $1,588\text{ cm}^{-1}$ corresponding to the reduced form of the GO and the intensity was drastically reduced at the HS condition due to the removal of the particle film (Fig. 12(b)). However, the Raman spectrum of the GO-ANS particles containing a wear track showed a characteristic G band peak at $1,586\text{ cm}^{-1}$ at a much higher intensity than the bulk particle (Fig. 2(a)) in both sliding speed conditions (Fig. 12(c)). The higher bulk Raman intensity confirms that the GO-ANS particles were effectively deposited on the wear tracks to form a sticky continuous thick protective film (Figs. 10(c) and 10(f)) and thereby provide lower and steady COF and wear behavior in both sliding speeds (Fig. 9).

The above discussion concludes that the capability of the solid nanoparticles to infiltrate the rubbing contact zone, the wettability, the surface interacting adhesion phenomena of the particles, and the thermal stability of the particles during sliding are key factors which decide the superior solid film lubrication properties of the materials along with demanding tribological parameters. Surface modification of the graphene oxide with ANS molecules exhibited better tribo-chemical properties and a wide range of solid lubricating phenomena. The attached ANS chains can react with the steel surface to form a tribolayer through

which the reduced graphene sheets can attach to the surface (Fig. 13). Under an applied load, these sheets may be pushed down to the bottom to form a thick particle film which will have high thermal stability, better adherence to the substrate to provide a low friction barrier. It is confirmed from the above discussion that amongst the prepared functionalized lubricant particles, the GO-ANS provides a unique friction and wear reduction pathway by utilizing surface-active adhesive phenomena and an enhanced thermal stability of the in-built tribofilm. These observations are of importance in designing lubrication systems for industrial applications as well as for boundary lubrication for conditions where wet lubricants are difficult to employ.

4 Conclusions

In dry tribological tests, the failure of adhesion of lubricant particles to the area of contact and their instability under shear results in high friction and wear during rubbing of steel on steel tribopairs. Functionalization with suitable organic functionalities facilitates the structural stability of the particles and assists the particles in adhering to the contact and helping to control the friction and wear. Herein, a simple

Fig. 12 Raman spectral study of tribo film generated with microtribological ball-on-disc experiments on worn disc tracks by (a) GO, (b) GO-ODA, and (c) GO-ANS particles in LS and HS ambient condition.

Fig. 13 A schematic showing a possible mechanism how GO-ANS particles can have better adherence to the contact and provide a low friction barrier.

route has been established to prepare functionalized graphitic particles through a nucleophilic addition reaction of ODA and ANS with GO nanosheets. FT-IR, UV-Vis, Raman, and XRD analyses suggest the successful reduction of the oxygen functionality of GO and the simultaneous covalent anchoring of the ODA/ANS chains on GO nanosheets. The presence of $-\text{SO}_3\text{H}$ and $-\text{OH}$ functionalities on the GO-ANS surface improved the wettability of the particles which is confirmed by water contact angle and DLS measurements. In contrast, after functionalization with ODA, the presence of long hydrocarbon chains makes the GO-ODA hydrophobic in nature.

In solid film lubrication, solid particles need to stay in the asperity zone during loading and shearing and form an antifriction transfer film through their adhesive bonding to the metallic substrate. In macro-tribological experiments, under high contact pressure (1.4 GPa) the functionalized particles are better able to control the friction due to the strong adhesion of the particles, since with increasing pressure the particles are pushed down in the contact region and adhere to the substrate to form a continuous film which eventually reduces the friction. Amphoteric GO-ANS provided a lower and consistent COF (0.06) over time compared to hydrophobic GO-ODA. This is because the hydrophilic groups and the sulfur-containing ANS chains on the GO facilitate better adherence to the steel surface. It was interesting to observe that although the GO particles provided lower COF similar to GO-ANS at initial sliding, over time, the performance of the film decreased and allowed the COF to rise to some extent due to its poor thermal stability. The results from microtribological tests at lower sliding speed support the macrotribological test results. With increasing sliding speed, graphite, GO, and GO-ODA exhibit higher friction due to poor adhesion and/or poor thermal stability. However, similar frictional behavior was observed for the GO-ANS in microtribological tests at both speed condition (LS and HS). GO-ANS consistently displayed the lowest COF among the GO particles in both speed conditions (0.08 for LS and 0.1 for HS) along with a lower wear depth and a significantly reduced wear track width. Significant improvement in friction and wear reduction of the GO-ANS is ascribed to the sulfur-containing ANS

chains, which may have superior surface-active adhesive properties. The superior adhesion of the GO-ANS along with an enhanced thermal stability enables the particles to assemble at the contact interface to form a thick protective tribofilm. The presence of this film is confirmed by Raman, FE-SEM, and corresponding EDS analyses. The film-forming abilities and low COF of the GO-ANS material show great potential as a solid lubricating advanced material for rotating and reciprocating tribosliding mechanical devices.

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