PREFACE

Tribology, the study of surfaces moving relative to one another and a phenomenon that affects our everyday activities in a multitude of ways encompasses three important aspects: friction, wear and lubrication. It is both technologically-relevant and scientifically-fascinating and finds applications in almost every industry such as machine elements, manufacturing processes, automotive, space, renewable energy and bio-tribology, to name a few. Tribology is particularly important in today's world because a vast amount of energy is lost in overcoming the friction in mechanical systems. Therefore, finding ways to minimise friction and wear by making use of the new surfaces, materials, and lubrication technologies are crucial to a greener and more sustainable world.

Out of the several techniques used to minimise the friction and wear, lubrication is the most widely used approach. Lubricants are formulated to meet the demands of a wide variety of applications, and the formulation begins with one or more mineral or synthetic base oils. Additives, which perform a variety of functions, including minimising the variation of viscosity with operating conditions, minimising boundary friction, increasing chemical stability, controlling contamination may be dissolved or suspended in the fluid. Liquid lubricants are extremely effective and are certainly the most widely used types of lubrication. However, there are some conditions or components where liquids may not be used, particularly those, where lightweight is important, and the loads are low, an interface can be lubricated by a gas. Solid lubricants are typical materials that provide low friction because of their inherent low shearing characteristics. For example, materials such as graphite, molybdenum disulphide, graphene and hexagonal boron nitride have layered structure and very low interlayer shear stress. Other solid lubricants are based on soft materials, such as noble metals, whose inherent resistance to shear stress is low. Although solid lubricants are not viable in some cases, the number and variety of applications using them, either solid or as an additive to a liquid, is increasing rapidly due to recent advancements in materials tribology.

Graphene, the first 2D material and a crystalline allotrope of carbon, is a single-atom-thick layer of graphite consisting of sp^2-hybridized carbon atoms arranged in a hexagonal lattice. Low interlayer shear stress, high chemical inertness, atomically smooth surface, high specific area, and excellent strength of graphene are the desirable properties from the tribological point of view. Graphene, as a solid lubricant reduces the friction forces between the contact surfaces on nano-, micro- and macro-scale. The solid lubrication effect of graphene is due to its lamellar structure with low interlayer shear strength. However, the potential of graphene as a lubricant both as a solid lubricating coating and as an additive in liquid is yet to be fully realised.

In view of the above, it becomes imperative to explore the potential of graphene as an effective lubricant. Hence, the present study has been carried out in two phases; (i) the examination of friction and wear properties of graphene coatings under dry sliding and (ii) the tribological performance of the graphene as an additive in water-based lubricant. The graphene coatings have been synthesised by thermal chemical vapour deposition on a nickel-catalysed bearing steel under different conditions of growth temperatures (650, 750, 850, and 950 °C), acetylene flow rates (6, 8, and 10 sccm), and reaction times (10 and 20 min) to determine the optimum conditions of growth. The tribological performance of graphene coatings, synthesised under optimum conditions have been investigated under unidirectional as well as reciprocating sliding against bearing steel ball by conducting tests at different loads and speeds. The base steel and nickel-plated steel have also been tested against the bearing steel ball under the same conditions to elicit the effectiveness of graphene in improving the tribological performance of self-mated steel pair. For unidirectional sliding, the disc has been set to rotate against the stationary counterpart (ball) with an average sliding speed of 0.07 m/s under an applied average load of 0.5 N for shorter as well as longer duration under atmospheric conditions. The tribological performance under reciprocating sliding has been examined by allowing the disc to reciprocate against the stationary counterpart (ball) with a frequency of 1 Hz (sliding speed of 0.01 m/s) over a stroke length of 5 mm under different applied normal loads (0.1, 0.3, 0.5, and 1 N). In order to explore the friction and wear behaviour of graphene oxide as an additive in water-based lubricant and to obtain the optimum amount of addition, different concentrations (0.01, 0.05, 0.1, and 0.5 wt. %) of graphene oxide have been dispersed in water and the performance of these dispersions has been evaluated for self-mated SS 304 disc-ball tribo-pair under reciprocating sliding using a ball-on-disc configuration at high contact stress (~1.42 GPa). Further, the influence of applied normal load and sliding speed has also been examined for the optimised concentration of graphene oxide in water and the prevailing mechanisms of wear have been established.

The present thesis has been organised in the six chapters, as summarised below:

Chapter 1 includes the introductory remarks highlighting the technological importance of the problem under investigation.

Chapter 2 begins with a critical review of the existing literature explaining the surface interactions and their consequences in the form of friction and wear of the surfaces. It is followed by a brief description of various techniques used to reduce friction and wear with a particular emphasis on the lubrication. A brief depiction of different types of lubricants (liquid, semi-solid, solid, and gaseous) has also been included along with a detailed presentation of properties and applications of some common solid lubricants. The chapter further highlights the structure, properties, applications, and methods of synthesis of graphene which is followed by an exhaustive review of literature regarding the chemical vapour deposition (CVD) of graphene, its types, and parameters affecting the CVD growth of graphene. A comprehensive presentation of the published literature emphasising the role of graphene in improving the tribological performance of a system has also been included in the chapter. The chapter ends with the presentation of the formulation of the problem.

Chapter 3 outlines the details of materials and experimental procedures used in the present study to explore the tribological performance of the synthesised graphene coating and graphene as an additive in water-based lubricant. In the current investigation, circular disc-shaped (ϕ 25 mm × 7 mm) specimens of bearing steel (GCr15) and stainless steel (SS 304), have been used as the substrates. A layer of nickel has been electroplated on the bearing steel surface to facilitate the graphene deposition. A thermal CVD (T-TCVDM-21, Technos Instruments, Jaipur, India) set-up has been used for the graphene deposition under different conditions of growth temperature (650, 750, 850, and 950 °C), acetylene flow rate (6, 8, and 10 sccm), and reaction time (10 and 20 min) with acetylene as a carbon source and hydrogen gas as a reducing medium. The high-resolution Raman spectroscopy has been employed to determine the optimum parameters of graphene growth, whereas X-ray photoelectron spectroscopy (XPS) and high-resolution transmission electron microscopy (HR-TEM) have been used for characterisation of the graphene films. The friction and wear characteristics have been examined under unidirectional as well as reciprocating condition for base steel, nickel-plated steel, and graphene-coated steel by sliding against a GCr15 steel ball of 6 mm diameter. For unidirectional sliding, the disc has been set to rotate against the stationary counterpart (ball) with an average sliding speed of 0.07 m/s under the applied normal load of 0.5 N, and tribological performance of graphene-coated bearing steel has been investigated for shorter (800 cycles) as well as longer (5600 cycles) duration. For reciprocating sliding, the disc has been set to reciprocate against the stationary counterpart (ball) with a frequency of 1 Hz (sliding speed of 0.01 m/s) over a stroke length of 5 mm under different applied normal loads of 0.1, 0.3, 0.5, and 1 N.

The chapter also includes the detailed procedure followed for the characterisation of graphene oxide (GO) and the formulation of graphene oxide-water dispersion having different concentrations (0.01, 0.05, 0.1, and 0.5 wt. %) of GO. The friction and wear tests have been conducted using a multi-functional tribometer at a normal load of 5 N employing a ball-on-disc geometry under reciprocating motion with a stroke length of 5 mm and sliding speed of 0.01 m/s for 3600 cycles with self mated stainless steel disc and ball as a tribo-pair to determine the optimum concentration. Further, friction and wear properties have been examined at different normal loads (5, 10, 15, and 20 N) and different sliding speeds (0.005, 0.01, 0.05, and 0.1 m/s) for the optimised concentration of graphene oxide in water. The testing has also been performed using pure water as a lubricant for the purpose of comparison. The details of techniques such as optical microscopy, Raman spectroscopy, scanning electron microscopy (SEM) equipped with energy dispersive spectroscopy (EDS), and transmission electron microscopy (TEM) used to characterise the worn surfaces have also been included in this chapter.

Chapter 4 begins with the results on the characterisation of bearing steel, nickel-plated steel, and multi-layer graphene coating on steel synthesised under different conditions of growth temperature, acetylene flow rate, and reaction time, to determine the optimum conditions. The thickness of the nickel layer over the bearing steel is ~ 25 μm as revealed by SEM. Raman spectra of graphene grown on surfaces under each condition show the presence of a D, G, and 2D peak mainly, at ~ 1350 cm^{-1}, ~ 1580 cm^{-1}, and ~ 2700 cm^{-1}, respectively, for each temperature. A decrease in I_D/I_G ratio with increasing temperature from 650 to 850 °C reflects an improvement in the quality of graphene with no significant change in I_D/I_G ratio beyond 850 °C. The lowest I_D/I_G and the highest I_{2D}/I_G ratios observed for a growth temperature of 850 °C indicate that it is the optimum temperature for growth of good quality graphene. Based on the effects of acetylene flow rate and reaction time on the growth of graphene at this temperature and their I_{2D}/I_G and I_D/I_G ratios, it has been inferred that a flow rate of 6 sccm and a reaction time of 10 min are good for depositing thinner graphene coatings.

The chapter also contains the results and discussion pertaining to the friction and wear behaviour of base, nickel-plated and multi-layer graphene-coated steel against GCr15 steel ball under both unidirectional and reciprocating sliding. For unidirectional sliding, the friction coefficient shown by the base steel-steel tribo-pair is the highest (~ 0.89), whereas that shown by the graphene-coated steel-steel tribo-pair is the lowest (~ 0.15). The friction coefficient observed for the nickel-plated steel-steel tribo-system is ~ 0.66. A significant reduction in coefficient of friction and wear observed for steel-multi-layer graphene-coated steel tribo-pair, has been attributed to the existence of graphene on the disc and the transfer of graphene to the counter surface which provides a low shearing interface between the mating bodies. The presence of graphene on the ball has been confirmed by Raman spectroscopy. The results on reciprocating sliding behaviour of multi-layer graphene-coated bearing steel under different normal loads of 0.1, 0.3, 0.5, and 1 N and sliding speed of 0.01 m/s show that both the coefficient of friction and the wear volume decrease with increasing load from 0.1 to 0.5 N and increase beyond that. The observed behaviour has been attributed to (i) homogenisation and smoothening of graphene coatings with increasing load and (ii) the transfer of graphene to the ball which inhibits direct contact between mating bodies and leads to a reduction in both friction and wear. However, an increase in the coefficient of friction and wear volume for a normal load of 1 N has been ascribed to the failure of graphene coating and initiation of direct metal-to-metal contact. The abrasion has been found to be the dominating wear mechanism for steel-graphene coated steel tribo-pair for both unidirectional and reciprocating sliding, while adhesion and wear induced oxidation is the associated mechanism for steel-steel and steel-nickel plated steel tribo-pairs. In the end, the results have been discussed to have a coherent understanding of the role of graphene coatings in affecting the friction and wear between the tribo-pair.

Chapter 5 includes the results on the characterisation of the stainless steel, graphene oxide powder, and its dispersion in water with different concentrations (0.01, 0.05, 0.1, and 0.5 wt. %). Atomic force microscope (AFM) and transmission electron microscope (TEM) reveal that the thickness of dispersed graphene nano-sheets is about 1.2 nm with a size smaller than 5 μm. The rheological characterisation reveals that the viscosity of water-graphene oxide dispersion increases with increasing amount of graphene oxide in water. The results on tribological behaviour under reciprocating sliding are presented in three parts: (i) effect of concentration on the tribological behaviour, (ii) effect of normal load on the tribological behaviour, (iii) effect of sliding speed on the tribological behaviour.

The friction and wear tests conducted to investigate the effect of the amount of graphene oxide in pure water on the macro-scale tribological performance of self-mated stainless steel tribo-pair at a normal load of 5 N and sliding speed of 0.01 m/s in ambient condition for 3600 cycles reveal a significant decrease in friction, even for the addition of a very small (0.01 wt. %) amount of graphene oxide in water. The decrease in coefficient of friction has been attributed to the formation of a tribo-layer of graphene oxide on both the ball and disc surface as confirmed by Raman spectroscopy and Transmission electron microscopy, which hinders the direct metal-to-metal contact. The average coefficient of friction and wear volume have been found to decrease with increasing amount of graphene oxide from 0.01 to 0.1 wt. % followed by a slight increase for 0.5 wt. %, indicating that 0.1 wt. % is the optimum content of graphene oxide under the conditions used in the present investigation. The lower and higher concentrations of graphene oxide have shown deterioration in lubricating performance either due to inadequate or excess amounts of graphene oxide in water, depending on the amount of addition of graphene oxide.

Further, the tests conducted at different normal loads of 5, 10, 15, and 20 N to explore the effect of load on the friction and wear behaviour of tribo-pair for the optimised concentration (i.e., 0.1 wt.%) at a speed of 0.01 m/s for 3600 cycles suggest an increase in both the average coefficient of friction and wear volume with increasing load. HRSEM micrographs reveal the damaged tribo-layer at relatively higher loads indicating a possibility of penetration of tribo-layer by the asperities of counterface ball giving rise to metal-to-metal contact and resulting in an increase in the coefficient of friction as well as wear volume. The tests conducted to investigate the effect of sliding speed on the friction and wear behaviour of tribo-pair for the optimised concentration of GO (i.e., 0.1 wt. %) in water at a load of 5N for a duration of 3600 cycles indicate a decrease in coefficient of friction and wear volume with increasing speed from 0.005 to 0.05 m/s, followed by a slight increase for 0.1 m/s, suggesting that a speed of 0.05 m/s is the optimum speed. The decrease in friction and wear with increasing speed up to 0.05 m/s has been attributed to the greater tendency of entrainment of graphene oxide between the contact pairs with increasing sliding speed due to better circulation of graphene oxide nano-sheets between the rubbing surfaces. However, an increase in the coefficient of friction and wear volume beyond 0.05 m/s has been ascribed to the discontinuous supply of lubricant between the rubbing surfaces due to its ejection from the sliding interface. Finally, the results have been discussed in the light of the observed behaviour to develop a coherent understanding of the role of graphene oxide as an additive in water in governing the friction and wear of the self mated steel pair.

Chapter 6 presents the major conclusions of the present study pertaining to (i) the synthesis of multi-layer graphene coating and its friction and wear performance under unidirectional as well as reciprocating sliding and (ii) the tribological potential of graphene oxide as an additive in water.