Synthesis, Characterization and Tribological Applications of Nanocomposites of Some 2D Nanomaterials

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All mechanical systems are greatly concerned about frictional losses. Such losses must be extensively limited to increase their service life and save energy. The ability to control friction at the nanoscale is a crucial area of research nowadays. In this regard, various additives, including organic compounds having heteroatoms, metal complexes, and nanomaterials, have been used to improve the efficiency of the lubricating oil. Zinc dialkyl dithiophosphates (ZDDPs) have long been regarded as highly versatile additives. However, their widespread use has been limited due to their negative impact on catalytic converters, affecting exhaust emission control. In response to environmental concerns, accepted standards and norms in the literature have imposed restrictions on additives containing sulfur, phosphorus, and sulfated ash (SAPS) to promote a healthier environment. As a result, the emerging field of tribology has gained momentum, focusing on nano lubricants as eco-friendly solutions.

Nanomaterials have become pivotal in lubricating oils as efficient antifriction and antiwear additives due to their unique properties, including high specific surface areas, small dimensions, and rapid tribological action. Various nanomaterial morphologies, such as nanoparticles (NPs), nanospheres, nanosheets (NSs), and quantum dots (QDs), have found diverse applications, contributing to the reduction of hazardous materials for human health and the environment. These nanomaterials offer substantial benefits in enhancing the performance, lifespan, and sustainability of mechanical systems by exhibiting remarkably low friction coefficients and wear rates.

The tribological activity of nanoparticles/nanospheres of various metals, including metal oxides, metal sulfides, and metal halides, is well-established. These nanomaterials

demonstrate their tribological effects through several mechanisms, which may involve tribosinterization, rolling, polishing, and tribofilm formation. These mechanisms can act individually or in combination to influence the overall tribological behavior of the materials. Two-dimensional nanomaterials, such as graphene, molybdenum disulfide, tungsten disulfide, graphitic carbon nitride, and hexagonal boron nitride, are known for their excellent lubricating properties due to their large surface area and weak van der Waals forces between adjacent layers.

In this current research, nano additives with exceptional tribological efficiency were developed using nanoparticles/nanospheres, nanosheets, and their composites. These nano additives were blended with paraffin oil, resulting in improved lubricity.

Therefore, during the current investigation, ternary nanohybrid of lanthanum doped yttria nanoparticle (La-Y_2O_3) with covalently functionalized graphene oxide, and molybdenum disulfide (MoS_2), nanocomposite of two different nanosheets, bismuth selenide (Bi_2Se_3) and N-doped bismuth tungstate (N-Bi_2WO_6), and binary composite of Co-doped manganese vanadate (Co-MnV_2O_6) nanosheets with nickel oxide (NiO) nanosphere have been prepared. The nano additives and their nanohybrids have been characterized by utilizing advanced analytical techniques, including scanning electron microscopy (SEM)/high-resolution SEM with energy-dispersive X-ray (EDX), transmission electron microscopy (TEM)/high-resolution TEM, X-ray diffraction, Fourier transform infrared spectroscopy (FT-IR), UV-visible spectroscopy, Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS).

The tribological performance of nano additives was assessed in paraffin oil (PO) using the ASTM D4172 and ASTM D5183 tests on a four-ball tester. These standardized tests provided valuable data on their friction-reducing and antiwear efficiencies.

The research findings indicate that the nanoparticle/nanosphere acted as spacers, effectively controlling the restacking of nanosheets and contributing to structural augmentation. In contrast, the heterogeneity of nanosheets prevented their agglomeration. Doped nanoparticles and nanosheets have improved the activity by generating defects.

The thesis comprises the following sections: Introduction, Experimental, Results and Discussion, Summary, and References.

Graphene is a two-dimensional hexagonal lattice of sp^2-hybridized carbon atoms, with each carbon atom forming sigma bonds with its three neighboring atoms and a perpendicular pi bond. Graphene oxide (GO), an oxidized form of graphene, contains oxygen-containing functional groups like epoxide, hydroxy, and carboxylic acid. As a result, GO has reduced sp^2 character and graphitic nature, leading to increased defects.

However, some drawbacks are associated with the lubrication of graphene oxide/reduced graphene oxide (GO/rGO), such as the tendency to agglomerate and restack nanosheets, limited ability to disperse in the lubricant, and weak adherence to interacting surfaces. Consequently, their load-bearing capacity, wear resistance, and friction-reducing properties are not commendable. The functionalization of graphene can be carried out covalently or non-covalently, or a combination of both to overcome these limitations.

Yttria has a cubic crystal structure. Doping with metal atoms as yttrium substitutes promotes the formation of defects, which affect the structure and eventually result in improved tribological properties.

The auto-combustion method was followed to prepare the yttria nanoparticles (Y_2O_3) and 7% lanthanum-doped yttria (La-Y_2O_3) nanoparticles. A hydrothermal method was adopted to prepare MoS_2 nanosheets using ammonium heptamolybdate. The graphene oxide was prepared by modified Hummer's method and further functionalized by methionine to form M-rGO. The addition of M-rGO to the binary composite (La-Y_2O_3)-MoS_2 resulted in the formation of ternary nanocomposite (La-Y_2O_3)-MoS_2-(M-rGO). The structure and morphology of all of the synthesized additives, nanosheets, nanoparticles/doped nanoparticles, and binary/ternary nanocomposites were investigated by the techniques Raman, powder XRD, HR-SEM with EDX, and TEM/HR-TEM. The chemical states of different elements in the ternary nanocomposite were studied by XPS. The dispersions of nanohybrids in the base oil were stable even after 48 h, as studied by UV/vis spectroscopy. The antiwear and antifriction efficiencies of the individual additives in base lube investigated on a four-ball tribo-tester according to ASTM-D4172 and ASTM-D5183 standards appear in ascending order Y_2O_3, MoS_2, M-rGO, and La-Y_2O_3. The La-Y_2O_3 nanoparticles and MoS_2 nanosheets exhibited enough tribological activity, but aggrandized activity is noted in the composite (La-Y_2O_3)-MoS_2. The lubricity of methionine functionalized rGO was well enhanced from the otherwise tribologically active GO nanosheets. The activity is much improved upon adding M-rGO to (La-Y_2O_3)-MoS_2. Thus, the robust synergy between nanoparticles and nanosheets has assured paramount efficiency. The wear track studies based on SEM and AFM authenticate the above gradation. The nanoparticles participated in improving lubrication via rolling, polishing, and mending mechanisms. Nanoparticles/doped nanoparticles have successfully reinforced the nanosheets of MoS_2/M-rGO, aided in segregating them from one another, and hindered them from getting re-piled. The nanosheets have successively countered the agglomeration of nanoparticles. The incredible tribological activity of the ternary composite (La-Y_2O_3)-MoS_2-(M-rGO) is accredited to intense interaction among the constituents as supported by XPS of the tribofilm.

Further, the 2D materials were chosen to design composites for extensive friction and wear reduction because of their inherent characteristics, specifically weak van der Waals forces between the proximal layers providing lubricating properties and their high dispersibility in base lube. The preparation of bismuth selenide and bismuth tungstate nanosheets was achieved hydrothermally. Bismuth tungstate nanosheets were introduced onto bismuth selenide to increase the tribological activity. The layered morphology of bismuth selenide and bismuth tungstate was instrumental in synergizing the activity of the composite. Hydrothermally synthesized nitrogen-doped bismuth tungstate was used to form the composite with bismuth selenide for further activity advancement. Appraisal of tribological activity based on the ASTM D4172 and D5183 tests revealed the tremendous significance of layered morphology and nitrogen doping in the results. HR-SEM and TEM examinations of Bi_2Se_3/Bi_2WO_6 and Bi_2Se_3/N-Bi_2WO_6 composites discern Bi_2WO_6/N-Bi_2WO_6 nanosheets physically adorning Bi_2Se_3 nanosheets. FT-IR, p-XRD, and XPS studies were used to characterize the as-synthesized nanomaterials. UV/visible spectroscopy technique has been used to investigate the dispersion stability of the nanomaterial blends in PO. Even after 72 h, the most stable system was Bi_2Se_3/N-

Bi_2WO_6. As per the tests mentioned above, the tribological assessment of the blends at the optimal concentration (0.05 percent w/v) demonstrated the best efficiency of Bi_2Se_3/N-Bi_2WO_6 in reducing friction and wear. The next was Bi_2Se_3/Bi_2WO_6, followed by N-Bi_2WO_6, Bi_2WO_6, and Bi_2Se_3. SEM and AFM analyses of the wear track support the above order of efficiency. According to the XPS study of the worn pathway in the presence of Bi_2Se_3/N-Bi_2WO_6, the tribofilm contains oxides of Bi, Se, W, and Fe_2O_3 and tungsten nitride leading to enhancement in the tribological efficiency. Doping nitrogen into bismuth tungstate led to the formation of defects, which improved lubricating characteristics. The phenomenal tribological activity of Bi_2Se_3/N-Bi_2WO_6 could be attributed to nitrogen doping and the hetero lamellar structure, which assisted in preventing restacking.

Furthermore, MnV_2O_6 (MVO) and Co-doped MnV_2O_6 (C-MVO) nanosheets were hydrothermally prepared to fabricate exceptionally tribologically efficient materials. The presence of weak van der Waals forces among the nanosheets seems to have a significant impact in the field of tribology. The wilful incorporation of Co as a dopant was aimed at exploiting its potential to augment tribological activity. Undoubtedly, the persistent issues of poor dispersion stability, weak adherence, and agglomerating tendencies of nanosheets exist; the solution to these problems is offered through the non-covalent functionalization of C-MVO nanosheets. MOF-derived NiO nanospheres, prepared through a hydrothermal process followed by calcination, were employed to enhance the tribological performance of C-MVO nanosheets through non-covalent functionalization. The prepared additives were examined using XRD, FT-IR, SEM/HR-

SEM, TEM/HR-TEM, and XPS. The HR-SEM and TEM studies of hybrid NiO/C-MVO revealed NiO nanospheres uniformly embedded amidst the layered C-MVO nanosheets. The ASTM D4172 and ASTM D5183 standard tests were used to evaluate the tribological properties of pure PO and its mixtures with additives MVO, NiO, C-MVO, and NiO/C-MVO at the optimum concentration of 0.050% w/v. The tribological data, including the coefficient of friction (COF), mean wear scar diameter (MWD), and seizure load, showed the following order of antiwear and antifriction efficiencies:

MVO < NiO < C-MVO << NiO/C-MVO

SEM and AFM investigations of the wear pathway corroborate the above claim. The composite of nanospheres with nanosheets has demonstrated efficient synergy in the hybrid. Combining the structural benefits of 2D C-MVO lamellae and 0D NiO nanospheres, this nanocomposite achieves a synergistic effect, enhancing tribology performance as a lubricating additive. During the tribological test, layered C-MVO nanosheets exhibit effective adsorption onto the surface of friction pairs, thereby preventing direct contact between them and significantly reducing wear. Introducing NiO nanospheres between the C-MVO layers transforms effectively sliding friction into rolling friction, substantially reducing the coefficient of friction (COF). Investigations of the wear track via EDX and XPS studies indicate the generated tribofilm comprised of lubricious metal oxides; Co_2O_3, V_2O_5, MnO_2, Mn_2O_3, NiO, Ni_2O_3 and metallic alloy Ni-Fe/Cr, which prevents metal-metal contact between sliding surfaces. As a result, the collaborative lubrication provided by C-MVO nanosheets and NiO nanospheres demonstrates outstanding antiwear and antifriction performance.

Finally, based on their significantly high tribological activity (compared to most of the published results obtained under similar test conditions), the nanocomposites studied in the present investigation may be recommended as potential wear and friction modifiers.