

Studies on Some Nanomaterials as Wear and Friction Modifiers



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By

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SUMMARY

All mechanical systems are greatly concerned about frictional losses. To increase their service life and save energy, such losses must be extensively limited. The ability to control friction at the nanoscale is a key area of research nowadays. In this regard, a variety of additives have been used to improve the efficiency of the lubricating oil. For their ability to reduce wear and friction, many lubricant additives, including organic compounds having heteroatoms, metal complexes, and nanomaterials have been studied in the literature. ZDDPs, which stand for zinc dialkyl dithiophosphates, are the most versatile additives. Nevertheless, their widespread use has been curtailed because of their propensity to reduce the effectiveness of catalytic converters for exhaust emissions. There are plenty of accepted standards norms in the literature which impose restrictions on the additives containing sulphur, phosphorus, and sulfated ash (SAPS) in order to maintain a healthy environment. Thus the need of green tribology, which is now an emerging field for tribologists, are fulfilled by nano lubricants. Nanomaterials have gained the utmost significance as effective antifriction and antiwear additives in lubricating oil because of their high specific surface areas, small dimensions, and quick tribological action. Nanomaterials with various morphologies, such as nanoparticles (NPs), nanotubes (NTs), nanosheets (NS), and quantum dots (QDs), have found a wide range of applications since they are environmentally friendly and reduce the usage of materials that are hazardous to both human health and the environment. The potential benefits of such materials in improving the efficacy, lifespan, and sustainability of mechanical systems have been extensively recognized due to their extremely low friction coefficients and wear rates.

SUMMARY

It is widely known that the nanoparticles/nanorods of several metals, such as metal oxides, metal sulphides, metal halides, etc., exhibit tribological activity through an array of mechanisms, including tribosinterization, rolling, polishing, and the formation of tribofilm, or a combination of these mechanisms. The large surface area and weak van der Waals forces between adjacent layers of two-dimensional nanomaterials such as graphene, molybdenum disulfide, tungsten disulphide, graphitic carbon nitride, and hexagonal boron nitride having great lubricating attributes. Therefore, in the present research, nanorods, nanosheets, and composites of nanosheets and nanorods have been used to develop nanoadditives with great tribological efficiency. The blends of synthetic additives were made in paraffin oil, and their tribological activity revealed improved lubricity. Therefore, during the current investigation, different 2D nanosheets such as graphitic carbon nitride ($g\text{-C}_3\text{N}_4$), metal organic frameworks (MOFs), and vanadium selenide (VSe_2) based nano lubricants, and their noncovalently functionalized nanohybrid with nitrogen doped zinc oxide (N-ZnO) nanorod, Mo-doped BiVO_4 nanorod, and porous La-doped zinc borate matrix have been prepared respectively. The nanoadditives and their nanohybrids have been characterized by employing scanning electron microscopy (SEM)/high resolution (HR) SEM with energy dispersive X-ray (EDX), transmission electron microscopy (TEM)/HR-TEM, X-ray diffraction, Fourier transform infrared, UV-visible, and X-ray photoelectron spectroscopy (XPS) techniques. Their tribological properties have been evaluated in paraffin oil using ASTM D4172 and ASTM D5183 tests on a four-ball tester. It has been observed that the nanosheets, in turn, prevented the agglomeration of the nanorods, while the nanorods functioning as spacers controlled the

restacking of the nanosheets and provided structural augmentation. Doped nanorods have improved the activity by generating defects. By acting as an intelligent oil reservoir that develops a self-lubricating system, the porous structure of the matrix plays a critical role in improving lubricating properties by allowing the pore structure for discharge of the base oil, which is already stored in pores, to the contacting surfaces consistently.

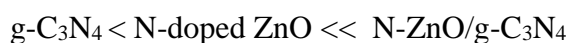
The thesis comprises the following sections: Introduction, Experimental, Results and Discussion, Summary, and References.

A carbon nitride polymer of high thermal stability possessing graphitic structure $g\text{-C}_3\text{N}_4$ with weak van der Waals forces amid the 2D-nanosheets appears to be very influential in the field of tribology. Though $g\text{-C}_3\text{N}_4$ has acquired an immense potential as a lubricant additive, poor dispersion stability, weak adherence, and agglomerating tendencies are always problematic. Functionalization of $g\text{-C}_3\text{N}_4$ non-covalently, provides a solution to these problems.

Zinc oxide has an open hexagonal crystal structure. Doping with different atoms as zinc or oxygen substitutes promotes the formation of defects, which affect the structure and eventually result in improved tribological properties.

The $g\text{-C}_3\text{N}_4$ nanosheets were prepared by heating melamine, followed by ultrasonication. The hydrothermal method was used to prepare N-doped ZnO nanorods. The hybrid of nanorods and nanosheets was prepared by ultrasonication. The techniques HR-SEM with EDX, TEM/HR-TEM, FT-IR, and powder XRD were applied to characterize the as-prepared nanomaterials. Nanorods morphology was identified for N-doped ZnO, which is ascribed to experimental conditions, time, temperature, heating rate, etc. The

morphology of hybrid reveals the nanorods spread between nanosheets and bonded to them via weak physical interactions. Examination of antiwear/antifriction activity (ASTM D4172 test) and load-bearing capacity (ASTM D5183 test) of the synthesized nanomaterials on a four-ball tester at the optimized concentration 0.20 %w/v reveals the order as given below-



The synergy between nanorods with nanosheets has worked efficiently in the hybrid. SEM and AFM studies of the wear pathway support the above statement. XPS studies of the wear track divulge that the tribofilm is composed of ZnO, adsorbed g-C₃N₄, and Fe₂O₃. The enhanced nanorod lubrication by a combined effect of tribosinterization and rolling mechanisms.

Further, in the next research work, ultrathin manganese-based 2D-metal organic framework nanosheets (Mn-MOF (U)) were synthesized by seizing the 3D growth in the presence of a strong sigma donating ligand triethylamine (TEA). Bulk Mn-MOF was synthesized by a similar method to Mn-MOF (U) without adding TEA in the solution. The thickness of the Mn-MOF (U) was determined to be 9 nm. The newly synthesized 2D-ultrathin MOF was found to show illustrious tribological performance in paraffin oil as manifested from its tribological data, namely MWD, COF, seizure load, and frictional power loss. EDX and XPS studies of the tribofilm on the wear track of steel ball supported the Mn-O-Mn and Mn-OH species, which clearly showed the transformation of the ultrathin MOF into a mixed valent manganese oxide (Mn²⁺, Mn³⁺, and Mn⁴⁺) structure. SEM and AFM studies of the worn surface exhibited highly improved smoothening than

paraffin oil alone. The tribological activity of Mn-MOF (U) showed apparent enhancement as compared to that of Mn-MOF (B). It could be correlated with the facilitated ease of sliding nanosheets in the former and restrained in the latter. Thus, the antiwear and friction-reducing mechanism of Mn-MOF (U) can be explained on the basis of the presence of weak van der Waals forces between the adjacent nanosheets in 2D materials, which promote their shearing under sliding motion.

Furthermore, nanoporous zinc borate (ZB) and, La-doped zinc borate (LZB) matrix were prepared using auto-combustion route willfully to take advantage of porosity and doping in enhancing the triboactivity. Assessment of tribological activity by ASTM D4172 test and ASTM D5183 tests divulged the effect of porosity and lanthanum doping on the observed results. Hydrothermally prepared VSe₂ nanosheets were used for the furtherance of the tribological activity of LZB. The HR-SEM and TEM studies of LZB/VSe₂ revealed VSe₂ nanosheets physically adhered to LZB. The as-prepared nanomaterials were characterized by p-XRD, FT-IR, and XPS. The tribological data based on the tests mentioned above for the optimized concentration (0.15 %w/v) of the test materials manifest the antiwear and antifriction efficiencies order follow as

$VSe_2 < ZB < LZB \ll LZB/VSe_2$

SEM and AFM studies of the wear track corroborate the above result. Analysis of the wear pathway by XPS reveals that the tribofilm comprises oxides of La, Zn, V, Se, B, and Fe₂O₃. Unambiguously, cooperative interaction between LZB and VSe₂ nanosheets governed the commendable tribo-activity of LZB/VSe₂.

SUMMARY

In the last investigation of this research, to pave the way for highly tribologically efficient 2D materials, Ni-Mn based bimetallic-organic framework (NMF) was synthesized ultrasonically. Considering further advancement of its activity, hydrothermally synthesized BiVO₄ (BV) / Mo-doped bismuth vanadate (MBV) nanorods were introduced to obtain nanohybrids; MBV/NMF. The TEM, HR-SEM, and HR-TEM investigations of the hybrid (MBV/NMF) divulge that Mo-doped BiVO₄ nanorods were spread over NMF nanosheets and strengthened them. Using ASTM D4172 and ASTM D5183 standard tests, the tribological performance of well-characterized nanomaterials, BV, MBV, NMF, and MBV/NMF, were assessed in paraffin oil (PO) at the optimal concentration, 0.1% w/v. The tribological data such as coefficient of friction (COF), mean wear scar diameter (MWD), and seizure load revealed the antiwear and antifriction efficiencies order fallow as

$$BV < MBV < NMF \ll MBV/NMF$$

Significantly better activity of NMF nanosheets than the nanorods possibly owing to weak van der Waals forces existing amid the lamellae. Certainly, the molybdenum doping has escalated the activity of BiVO₄ nanorods. The hybrid MBV/NMF exhibited highly advanced activity because of non-covalent synergistic interactions between nanosheets and nanorods. Tribological findings of wear track were validated by the SEM and AFM. Investigations of the wear track via EDX and XPS studies indicate the generated tribofilm comprised of lubricious metal oxides; MoO₃, Bi₂O₃, V₂O₅, MnO₂, Mn₂O₃, NiO, Ni₂O₃, and metallic alloy Ni-Fe/Cr, which prevents metal-metal contact between sliding surfaces and thus synergetically improved the lubricity.