TRIBOLOGICAL STUDIES OF SOME NANOMATERIALS AND N, O CONTAINING FUSED HETEROCYCLIC RING SYSTEMS

THESIS SUBMITTED IN PARTIAL FULFILLMENT FOR THE AWARD OF DEGREE

DOCTOR OF PHILOSOPHY

By

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Kavita

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CONTENTS

Abbreviations

AFM	Atomic force microscopy
ASTM	American society for testing and materials
BN	Boron Nitride
CNTs	Carbon nanotubes
COF	Coefficient of friction
DFT	Density Functional Theory
DMF	**N,** N-dimethylformamide
DMSO	Dimethyl Sulfoxide
EDX	Energy Dispersive X-ray Spectrometry
FE-SEM	Field emission- Scanning electron microscopy
FMO	Frontier Molecular Orbital
FT-IR	Fourier transforms infrared spectroscopy
g-C_3N_4	Graphitic carbon nitride
GO	Graphene Oxides
HOMO	Highest Occupied Molecular Orbital
KBr	Potassium bromide

LAMMPS	Large-scale atomic/molecular massively parallel simulator
LUMO	Lowest Unoccupied Molecular Orbital
MAPS	Materials and Processes Simulations Platform
MD	Molecular dynamics
MNDO	Modified Neglect of Diatomic Overlap
MoS_2	Molybdenum disulfide
MWCNs	Multi -walled carbon nanotubes
MWD	Mean wear scar diameter
MWV	Mean wear scar volume
NMR	Nuclear Magnetic Resonance
NPs	Nanoparticles
PANI	Polyaniline
PO	Paraffin Oil
PPESK	Poly Pthalazinone ether sulfone ketone
PPz	Pyranopyrazole
PTFE	PolyteraFluoro Ethylene
RDF	Radial distribution functions

RTIL	Room temperature ionic liquid
SAED	Surface area electron diffraction
SAPS	Sulphur Phosphorus Sulphated Ash
SDS	Sodium dodecyl sulfate
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
THPP	Tetrahydropyrazolopyridines
WS_2	Tungsten disulfide
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray powder diffraction
ZDDP	Zinc dialkyldithiophosphate

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Friction between the surfaces in relative motion results in energy loss because of the release of frictional heat. The phenomenon is also associated with loss of mass as surface wear. Lubrication is the only remedial measure to safeguard such proximal surfaces. Sundry lubricant systems with numerous types of additives, therefore, have been fabricated to address the issue. Among them, heterocyclic organic compounds, metal complexes, nanoparticles, lamellar structures, and composites find paramount significance. Conventional heterocyclic compounds containing heteroatoms, specifically nitrogen and oxygen, are categorically advocated for their friction/wear-lowering disposition due to their high miscibility in base oils and significant adsorption over the metal/alloy surface through the lone pair of electrons at heteroatoms and the aromatic ring electrons. Though fused benzene ring systems have been studied well for their friction and wear-reducing properties, fused heterocyclic systems have been rarely studied. Nano lubricants, colloidal suspensions of nano-size materials, are well appreciated for their dexterous antiwear behavior due to their small size and swift action. Because of high thermal conductivity, these lubricants enhance heat dissipation caused by friction. In the present investigation, some fused heterocyclic ring systems and paraffin oil-based nano lubricants have been prepared. Their tribological properties have been evaluated using a four-ball tribo-tester. The thesis is presented under major heads; Introduction, Experimental procedures, Results & Discussions, Summary, and References.

Chapter 1 introduction describes at first tribology, an essential field related to the endurance of mechanical systems. A brief account of the three crucial pillars of tribology, friction, wear, and lubrication, has been presented. Lubrication regimes, lubricants, their classification, types of additives in general, and antiwear/antifriction additives, in particular, are also included in this chapter. A critical literature survey has been provided on conventional organic compounds and nanomaterials as antiwear/antifriction additives.

The statement of the problem has been categorically depicted. At last, the aims and objectives of the current investigation have been defined.

Chapter 2 narrates the details of instrumentations used for various techniques such as Fourier Transform infrared spectroscopy (FTIR), electronic absorption spectroscopy (UV/visible), scanning electron microscopy (SEM)/high-resolution scanning electron microscopy (HR-SEM) with energy-dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM)/high-resolution transmission electron microscopy (HR-TEM), powder X-ray diffraction(p-XRD), and X-ray photoelectron spectroscopy (XPS) to characterize the synthesized additives and lubricated surfaces as well. A brief description of tribological parameters, mean wear scar diameter (MWD), coefficient of friction (μ), mean wear volume (MWV), wear rate, load-bearing capacity, and frictional power loss (P) has been furnished. The steel ball bearing specifications, paraffin oil characteristics, and tribological test procedures, namely ASTM D4172, ASTM D5183, wear rate determination, and wear scar surface examination, have also been included in this chapter.

The inferences derived from the results and discussion of the observed data have been laid out into four chapters, 3-6.

Chapter 3 illustrates the synthesis of a fused heterocyclic ring system, tetrahydropyrazolopyridines (THPP-H), with substituents methoxy (THPP-OMe) and the methyl (THPP-Me) by the one-pot multi-component reaction. NMR spectroscopy (^{1}H and ^{13}C) was used to authenticate the synthesis. Density Functional Theory (DFT) calculations fully agreed with the results obtained from tribological experiments.

Chapter 4 includes synthesizing and characterizing substituted pyranopyrazoles (PPz-R, where R=H, methyl, and methoxy), another fused heterocyclic ring system. Their tribological properties were evaluated. The interaction of the best additive, PPz-OMe, with

a borate ester (Vanlube 289) increased the efficiency synergistically. Results of DFT calculations and adsorption energies found using molecular dynamics (MD) simulations correlated very well with the experimental data.

Chapter 5 addresses the synthesis and characterization of vanadium pentoxide nanosheets, polyaniline (PANI), and polyaniline intercalated vanadium pentoxide nanosheets, PANI-$V_2O_5.nH_2O$ (PVO). The tribological data show notable improvement in the lubricity of base oil in the presence of PVO compared to V_2O_5 and PANI.

Chapter 6 contains the synthesis and characterization of graphitic carbon nitride (g-C_3N_4) nanosheets, lanthanum orthovanadate nanoparticles in the monoclinic phase (m-$LaVO_4$) and the composite g-C_3N_4/m-$LaVO_4$.The tribological data of the nanocomposite showed significant advancement in activity, which could be ascribed to the synergy between noncovalently interacting nanoparticles (m-$LaVO_4$) and nanosheets (g-C_3N_4).