INVESTIGATIONS ON REDUCED GRAPHENE OXIDE-BASED NANOHYBRIDS AS FRICTION AND WEAR MODIFIERS

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Zinc oxide has a hexagonal open-type crystal structure, which facilitates the formation of defects through doping. These defects result in the formation of slip systems and lower shear strength. Zinc oxide (ZnO) and magnesium-doped zinc oxide nanoparticles, $Zn_{0.88}Mg_{0.12}O$ (ZMO), were prepared by the auto-combustion method. Further, nanocomposites of the as-prepared nanoparticles with microwave-synthesized reduced graphene oxide (rGO) nanosheets, ZnO-rGO and ZMO-rGO have also been prepared with a view to see the effect of doping of magnesium in zinc oxide on the tribological properties of the nanocomposite. Triboactivity of the additives has been interpreted considering the parameters mean wear scar diameter, coefficient of friction, load-carrying capacity, and wear rates obtained from ASTM D4172 and ASTM D5183 tests at an optimized concentration (0.125% w/v). The performance of base lube and its admixtures have been found to lie in the order:

ZMO-rGO > ZnO-rGO > ZMO > ZnO > rGO > PO.

Outstanding enhancement in the triboactivity of nanocomposites, particularly that of ZMO-rGO, indicates that nanoparticles are irrefutably instrumental in the reinforcement of rGO. On the other hand, rGO is associated with the abatement of the agglomeration of the nanoparticles. Thus, interactions between rGO and nanoparticles are vehemently synergic in nature. It is noteworthy that the best results were obtained with the following optimized concentrations: ZnO/ZMO 0.25%, rGO 0.15%, and composites 0.125% w/v. Morphological studies of the wear track lubricated with different additives have been performed using SEM and contact mode atomic force microscopy. The results are in conformity with the order given

above. The EDX analysis of ZMO-rGO exhibits the presence of zinc and magnesium on the worn surface, supporting their role in the formation of in situ tribofilm. Their role is further corroborated by XPS studies.

Further, it was found engrossing to dope zinc oxide nanoparticles with two different ions in different oxidation states expecting more defects but retaining its wurtzite structure and see the effect on tribological activity. Correspondingly, zinc oxide was doped with yttrium and vanadium since yttrium oxide and vanadium oxide are both known to show tribological properties. Among the graphene-based polymer nanocomposites, recently, polyaniline functionalized graphene oxide has been shown to possess excellent tribological activity. Therefore, chemical functionalization of reduced graphene oxide has been achieved by polyaniline (PANI-rGO), and further by yttrium -vanadium co-doped zinc oxide nanoparticles to yield Y-V-ZnO/PANI-rGO. The tribological activity of various additives in paraffin oil using a four-ball tester at the optimized concentration, 0.005% w/v has been found in the following order:

Y-V-ZnO/(PANI-rGO) > Y-V-ZnO > V-ZnO > Y-ZnO > PANI-rGO > ZnO > PANI > rGO

It is conspicuous from the obtained results that the doping of vanadium and yttrium together in zinc oxide has enhanced the tribological activity, and further functionalization of PANI-rGO by Y-V-ZnO has influenced tribological activity synergistically. SEM and AFM Analysis of the wear-pathway validate the tribological results. The EDX spectrum of Y-V-ZnO/PANI-rGO is indicative of the presence of carbon, nitrogen, oxygen, vanadium, zinc, and yttrium on the wear scar surface, which authenticates their contribution in tribo-chemical film. The XPS studies of the worn surface divulge the constituents of tribofilm mainly as the tribo-sintered oxides of V, Fe, Zn, and Y along with adsorbed graphene.

Zirconia and 10%, 20%, and 30% cerium-doped zirconia nanoparticles (ZCO), ZCO-1, ZCO-2, and ZCO-3, respectively, were synthesized using the auto-combustion method. Binary nanohybrids, ZrO_2/rGO, ZCO-2/rGO, and ternary nanohybrids, ZrO_2/rGO/MoS_2, and ZCO-2/rGO/MoS_2 have been prepared with an anticipation of a fruitful synergic effect of rGO, MoS_2, and cerium-doped zirconia on the tribo-activity. Tribo-activity of these additives at the optimized concentration, 0.125% w/v follows the order:

ZCO-2/rGO/MoS_2 > ZrO_2/rGO/MoS_2 > ZCO-2/rGO > ZrO_2/rGO > MoS_2 > ZrO_2 > rGO > PO.

Thus, the results acknowledge the synergic effect of cerium-doped zirconia and lamellar nanosheets of rGO and MoS_2. There is non-covalent interaction among all individuals. Analysis of the morphological features of wear-track carried out by SEM and AFM of PO and its formulations with various additives is consistent with the above sequence. The EDX spectrum of ZCO-2/rGO/MoS_2 indicates the existence of zirconium, cerium, molybdenum, and sulfur on the wear-track, confirming, thereby, the active role played by these elements during tribofilm formation. The XPS studies of worn surface reveal that the tribofilm is made up of rGO, zirconia, ceria, and MoS_2 along with Fe_2O_3, MoO_3, and SO_4^{2-} as the outcome of the tribo-chemical reaction.

Furthermore, Phthalocyanine (Pc), a 16-membered macrocyclic ligand, comprises four isoindole units linked together by nitrogen atoms. It has two-dimensional geometry possessing a conjugated system of 18 π electrons that provide remarkable thermo-oxidative stability. Pc, because of extensive conjugation, has numerous applications in various technological fields. The role of the π-electron system is of utmost significance in charge-carrier transport-related properties, while the planar structure renders importance in the field of lubrication. Metal complexes resulting from deprotonation of the Pc ligand have been acknowledged in emerging research areas, including lubrication.

Covalent functionalization of graphene oxide (GO) was performed by 2-aminoethyl diphenyl borate (ADB). ADB was deliberately chosen to outreach the benefits of the enhanced lubrication by in situ formed boron nitride (BN) during tribological testing due to boron-nitrogen synergy. Nucleophilic attack of the -NH_2 group of ADB opened epoxide rings of GO, forming -NH-C-C-OH and simultaneously reducing GO to rGO. The product, therefore, is represented as ADB-rGO. For the betterment of lubricity, further non-covalent functionalization was also considered using triboactive phthalocyanine (Pc) or copper (II) phthalocyanine (CuPc). Based on the results of molecular dynamics and tribological tests in paraffin oil (PO), CuPc was preferred over Pc. Configurations of the adsorbate CuPc on the surface reveal that CuPc tends to fold/unfold upon adsorption. Thus, the CuPc nanotubes (NTs) were used for the non-covalent functionalization of ADB-rGO. The tribological activity of different additives at concentration 0.05% w/v reveals the order for antiwear/antifriction efficiencies and reduction in wear rates as:

CuPc-(ADB-rGO) > CuPc NTs > Pc > ADB-rGO > GO > PO.

Thus, CuPc-(ADB-rGO) overpowered the demerits of GO. The morphology of the surface lubricated with GO, ADB-rGO, was studied using SEM and AFM (contact mode). EDX analysis of the steel surface in the presence of CuPc-(ADB-rGO) divulges the additional elements boron, nitrogen, and copper in the in situ formed tribofilm, highlighting their active role in improving the tribological activity. XPS studies of the tribofilm show boron nitride, boron oxide, iron oxides, cupric oxide, and graphitic compounds. The synergic performance of layered structures rGO, CuPc, and in situ formed boron nitride validated the spectacular tribological performance of CuPc-(ADB-rGO).