

ABSTRACT

Globally, continuous depletion of the crude oil reserves, their increasing demand, and their hazardous environmental impacts together make the situation too awful for the coming generation. Also, the petroleum based stock worsening our eco-system during its whole lifespan and even after dumping. These oils are not degradable with time, therefore left their negative impact on eco-system for a prolonged time. Consequently, it is necessary to move towards green lubricants. Vegetable based biolubricants as an alternative to the petro-product is explored as a renewable source. Still, the petro-products are not entirely replaced by the biolubricants due to the limitation in the tribo-performance.

The present work focused on developing environment friendly lubricant which must be able to replace the petroleum-based stock. The biolubricants are designed in such a way that it can perform at least equal or better than petro-products. And, equipment can give its optimum performance by keeping the environment healthy. It known that any petroleum base stock, synthetic hydrocarbons and vegetable oils in pure form cannot fulfil all the required characteristics of lubrication criteria set by the equipment/engine's manufacturer. Therefore, the use of a small amount of additive in the base oil provides substantial changes in its tribo-properties. Nowadays, nanotechnology is a progressive step in lubricant formulation and many other fields.

In this study, initially, seven types of biolubricants i.e., castor, sunflower, cottonseed, sesame, rapeseed, olive and neemseed oils were chosen (without additive) for tribological evaluation. And, the role of their fatty acid structure studied on the tribo-performance. From their physical and thermo-oxidative properties, three raw oils, i.e., castor, rapeseed and sunflower oils were further explored with different types of additives

for the tribological tests (i.e., antiwear, antifriction and extreme-pressure evaluation). The tribological tests were examined as per the ASTM standards. In this study, the synthesized/selected nano-additives were calcium-copper-titanate (CCTO; synthesized with sol-gel method), modified copper oxide (S-CuO), cerium oxide (CeO₂) and polytetrafluoroethylene (PTFE). The tribo-performance of all these additives in the selected biolubricants investigated with four-ball tester with varying the concentration (0.1 to 1.0%w/v). The multifunctional chemical reagent zinc dialkyldithiophosphate (ZDDP) was also used in the base oils as an additive for comparing the tribo-performance with different nano-additives. Furthermore, all the additives were examined in similar concentrations with the commercially available paraffin oil. In general, the antiwear, antifriction and extreme-pressure behaviours reviewed from wear scar diameter (WSD), variation in mean coefficient of friction (COF), and load carrying capacity respectively. It was found that the lower concentration range (i.e., 0.1 or 0.25%w/v) of each nanoparticles exhibit improvement in antiwear properties, while deteriorated at higher concentration range (i.e. 0.5%w/v or more). On the contrary, extreme pressure behaviour improved at higher concentration range in most of the cases. A new hypothetical model was proposed presenting the role of the substrate surface and sub-surface to improve the tribo-performance. Other mechanisms like a real area of contact, nano-bearing effect, mending action, adsorbed and ordered layer phenomena also discussed in detailed.

The main shortcomings of biolubricants are oxidation stability and low temperature performance, which limits their widespread use. Therefore, the chemical modification of the base oil was performed by the epoxidation process to remove C=C reaction site and formation of the epoxy group. After the epoxidation, the obtained oils were also compared with all the selected additives. And, tribo-performances compared with the

similar level of additive compositions with the selected base oils. The compatibility of the nano-additives also measured with a different category of the oils. In most of the cases, CeO₂ and PTFE show better antiwear and antifriction behaviour as compared to S-CuO nano-additive either in unmodified and epoxidized oils. PTFE shows independent behaviour in case of extreme pressure test with all the base oils at any concentration. Also, the concentration of each nano-additive optimized in both unmodified and modified oils.

Different analytical tools like scanning electron microscope (SEM), energy dispersive spectroscopy (EDS), transmission electron microscope (TEM), atomic force microscope (AFM), X-ray diffractometer (XRD), nuclear magnetic resonance (NMR), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), gas chromatography mass spectroscopy (GC-MS) were used in this study for the characterization of the tested samples.