Chapter-7

Conclusions and scope for future work

This chapter concludes the key findings of the present work. It summarizes the synergistic effect and compatibility of the different base oils with different nano-additives. The scope for the future work ends this chapter.

7.1. Conclusions

This dissertation focused on developing environment benign additive based nanolubricants for meeting the specific requirements under sliding contact situations. Initially, different vegetable based biolubricants (castor, rapeseed, sunflower, neemseed, cottonseed, olive, and sesame) opted as a base lubricant to evaluate tribo-performance. And, the influence of fatty acid composition observed. The tribological tests (antiwear, antifriction and extreme-pressure) performed with four-ball test rig as per the ASTM standard.

In the next part of work, a small amount of additives (CCTO, S-CuO, CeO_2, PTFE, and ZDDP) were used in varying concentration range (i.e., 0.1, 0.25, 0.5 and 1.0%w/v) in the selected base lubricants separately to evaluate the tribological performance. Thereafter, selected biolubricants were chemically modified with epoxidation process to change the structure of fatty acid chain. It improved the low temperature performance and thermo-oxidative stability of the base lubricants. A similar level of nano-additive concentration was also used with the epoxidized oils to formulate the nanolubricants and compare the tribological results with the unmodified lubricants with/without additives. Commercially used paraffin oil was also used as base lubricant and also tested at similar concentration for the comparative study. The major conclusions of the work summarized in the subsequent sections:

7.1.1. Fatty acid structure of the biolubricants before and after epoxidation

Biolubricants in raw condition

The fatty acid composition of each explored biolubricants (castor, rapeseed, sunflower, neemseed, cottonseed, olive, and sesame) obtained with the GC-MS analysis. The composition and thermal stability properties of the biolubricants were as follows;

- GC-MS result exhibits that castor oil has lowest saturated fatty acid as 4% while it possesses a higher amount of mono-unsaturates (oleic acid + ricinoleic acid) as 88.9%.
- The highest saturation (about 37%) observed with neemseed oil.
- Poly-unsaturation was observed from minimum 6.8 to maximum 51.9% for castor and cottonseed oil respectively.
- A specific variation observed for oleic acid (C18:1) and linoleic acid (C18:2) content in biolubricants, however, other content varied randomly. Oleic acid shows increasing while linoleic as decreasing trend. (Sequence of oil: cottonseed, sesame, neemseed, olive, rapeseed, sunflower and castor oil)
- TGA analysis of the base biolubricants shows castor, rapeseed, and sunflower oils have higher decomposition temperature (approx. 400°C or more) measure with the help of the onset temperature (T_{onset}).

Biolubricants after epoxidation

The biolubricants were modified by the epoxidation method to alter the C=C (active sites for various reactions) structure into oxirane ring. The physical properties of the epoxidized oils were as follows:

- The significant increment in the dynamic viscosity of the base oils observed after the epoxidation. It may be due to the presence of the epoxy group.
- The dynamic viscosity of the epoxidized castor, rapeseed and sunflower oil was increased from 0.28, 0.089 and 0.076 to 0.502, 0.153 and 0.196 N-s/m^2 respectively.
- The slight change in the low temperature behavior of the epoxidized biolubricants also observed. Pour point temperature of the epoxidized castor, rapeseed, and sunflower oil increased from -33, -29 and -18°C to -37, -31 and -18°C respectively.

7.1.2. Dispersion stability of nano-additives in various lubricants

- SDS was used as a dispersant to improve the suspension stability of CCTO, CeO_2 and PTFE nano-additives in the different base oils.
- In case of CuO nanoparticles, the surface treatment method adopted. And, the SDS was capped over CuO to form S-CuO. This is because the CuO nano-additives were showing rapid agglomeration (visual inspection) than other nanoparticles.
- It observed that after the ultrasonication, all nanolubricants showed the uniform suspension for at least 48 hours.
- The initiation of agglomeration of the nanoparticles in various oils was different. And epoxidized oil has shown better nano-additive suspension stability than that of unmodified oils. It may due to increase in viscosity after the epoxidation.

7.1.3. Effect of nanolubricants on tribological properties

Table 7.1 shows whether any improvement observed in the tribo-properties or not, irrespective of the nano-additive concentration.

Table 7.1. A comparative summary of the overall study.

Oil composition	AW↑	AF↑	EP↑	Compatible	Remarks
CO+ CeO_2	✓	✓	✓	Y	Overall tribo-performance was improved.
ECO+ CeO_2	✓	✓	✓		
RO+ CeO_2	✓	✓	✓	Y	
ERO+ CeO_2	✓	X	✓		
SO+ CeO_2	✓	✓	✓	Y	
ESO+ CeO_2	✓	✓	NT		
CO+ S-CuO	✓	✓	✓	Y	1. Beneficial effect with CO and RO. 2. Not compatible with all.
ECO+ S-CuO	✓	~	X		
RO+ S-CuO	~	✓	✓	Y	
ERO+ S-CuO	X	✓	✓		
SO+ S-CuO	X	✓	✓	N	
ESO+ S-CuO	X	X	NT		
CO+ PTFE	✓	✓	X	Y	1. Good for AW and AF. 2. Independent for EP.
ECO+ PTFE	✓	✓	X		
RO+ PTFE	✓	✓	X	Y	
ERO + PTFE	✓	✓	X		
SO+ PTFE	✓	✓	X	Y	
ESO+ PTFE	NT	NT	NT		
CO+CCTO	✓	✓	✓	Y	Overall good tribo-performance.
PO+CCTO	✓	✓	✓	Y	
CO+ ZDDP	✓	X	✓	Y	AW and EP: Good. Not Eco-friendly.
PO+ ZDDP	✓	✓	✓	Y	

↑: improve, Y: yes, N: no, AW: antiwear property, AF: antifriction property, EP: extreme pressure property, NT: not tested, ✓: good tribo-performance observed, **X**: improvement not observed, and ~ : minute improvement.

The antiwear and extreme-pressure performances optimized on the basis of wear scar diameter size on the tested ball specimen (AISI 52100) and load carrying capacity respectively. Also, COF recorded automatically during the test run. The overall comparative improvement in antifriction and antiwear performance summarized in Table 7.2.

The tribo-performance conclusions were as follows:

- On the basis calculated film thickness and the topography of the worn surfaces lubricated with the base oils, it observed that the system is working in the boundary lubrication regime.
- For pure biolubricants, the antiwear results correlated with the composition of the biolubricants. And, it found that the C18:1 and C18:2 have a significant role in achieving the wear behavior of the biolubricants. In other words, the antiwear behavior is the function of C18:1 and C18:2.
- For nanolubricants, the best antiwear performance obtained at lower concentration range (i.e. 0.1 or 0.25%w/v) in most of the cases. Beyond this concentration level, the material loss was substantial and impaired performance noticed.
- ZDDP shows excellent compatibility with the castor oil and significant improvement in the antiwear and extreme-pressure properties were obtained. However, antifriction properties impaired at all the concentrations.
- Antifriction results show the direct proportional relation with the WSD variation in most of the cases. Also, lower interfacial stress obtained for nanolubricants at either concentration for different oils. Lower interfacial shear stress indicates better lubrication property.

Table 7.2. Overall summary of antiwear and antifriction improvement.

Composition	Antiwear Performance		Antifriction performance	
	Improvement (%)	Concentration (%w/v)	Improvement (%)	Concentration (%w/v)
CO+CCTO	26.9	0.25	6.4	0.1
CO+ S-CuO	24.04	0.1	34.6	0.1
CO+CeO_2	33.93	0.25	43.3	0.25
CO+PTFE	31.46	0.1	63.4	0.5
ECO+ S-CuO	16.85	0.1	Negligible	-
ECO+CeO_2	19.57	0.1	25.4	0.1
ECO+PTFE	28.1	0.5	58.2	0.5
RO+ S-CuO	9.84	0.1	70.0	0.1
RO+CeO_2	16.72	0.1	74.5	0.1
RO+PTFE	48.75	0.1	62.57	0.1
ERO+ S-CuO	Negligible	-	65.5	0.1
ERO+CeO_2	8.24	0.1	Impaired	-
ERO+PTFE	16.1	0.5	10.3	0.1
SO+ S-CuO	Negligible	-	52.8	0.1
SO+CeO_2	21.0	0.1	22.3	0.1
SO+PTFE	8.56	0.5	29.1	0.5
ESO+ S-CuO	Impaired	-	Impaired	-
ESO+CeO_2	20.6	0.1	11.7	0.1
PO+CCTO	38.3	0.25	17.2	0.25
PO+ S-CuO	22.2	1.0	17.1	1.0
PO+CeO_2	26.12	0.25	29.6	0.25
PO+PTFE	Impaired	-	7.5	0.1

- A small amount of the nanoparticles (from 0.1 to 1.0%w/v) were able to reduce the friction and wear significantly. Especially, PTFE and CeO_2 were found best additives at a lower concentration to compete for the ZDDP.
- Epoxidation of the biolubricants improved the oxidation stability. After the epoxidation, the base oil itself improved the antiwear and antifriction properties substantially.
- The addition of small amount of additive in epoxidized oil also shows some improvement, except S-CuO nanoparticles.
- Extreme-pressure property for modified oils was almost similar to the unmodified nanolubricants.
- In the extreme-pressure test, higher concentration ranges of the oxide nanoparticles (0.5 or 1.0%w/v) improved the load carrying and weld load performance. The maximum last non seizure load for pure oil and nanolubricants were 126 and 160 kgf, while weld load 160 and 200 kgf respectively. However, PTFE is independent of these criteria and show similar behaviour as base oil at all concentrations.
- Load carrying performance of the biolubricants with nano-additives shows at par performance to the paraffin oils also.
- The comparative tribological study reveals that additive based biolubricants can perform at par with the paraffin oil compositions. Thus the vegetable based nanolubricants are found to be a suitable alternative to the mineral oils.

7.1.4. Overall general conclusion

- *Compatibility:* All the nanoparticles are not compatible with the base oils to improve tribological performance.

- *Nanoparticle concentration effect:* Vegetable based biolubricants have shown higher concentration sensitive behavior as compared to paraffin oil.
- *Nanoparticle morphology effect:* The tribo-performances of the nanolubricants with the particles having lower aspect ratio were found better as compare to a high ratio. i.e.

  Spherical shape > Regular shape > Irregular shape.

7.2. Scope for the future work

The present work provides the detail insight about the biolubricants potential for tribological contact situations. Still plenty of work can be done in future. It includes:

- ❖ The effect of temperature and load variation on biolubricant's tribo-performance with/without nanoparticles can examine.
- ❖ The tribological evaluation of the nanoparticle based biolubricants can be performed on the test rig with conformal contact situations like pin-on-disc at different sliding speed and temperature.
- ❖ Synthesis of doped nanoparticles or development of the completely biodegradable additives. And, these synthesized additives can be used in biolubricants to keep the environment healthy even after disposal.
- ❖ Nano-additive based bio-greases can be developed for semi-solid lubrication conditions. In this case, epoxidized oil can be used as base oil.