PHYSICO-CHEMICAL STUDIES OF POLYMERIC LUBRICANTS

A Thesis Submitted to the
Indian Institute of Technology, Delhi
For the Degree of
DOCTOR OF PHILOSOPHY

BY

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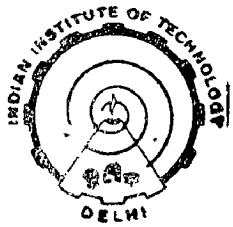

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DEDICATED

TO

MY PARENTS

C E R T I F I C A T E

This is to certify that the thesis entitled **Physico-Chemical Studies of Polymeric Lubricants** being submitted by **Mr. Sunil Kumar Sharma** to the Indian Institute of Technology, Delhi for the award of Degree of **Doctor of Philosophy** in Tribology, is a record of bonafide research work carried out by him. Mr. Sunil Kumar Sharma has worked under our guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to our knowledge, has reached the requisite standard.

The results contained in this thesis have not been submitted, in part or in full, to any other University or Institute for the award of any degree or diploma.

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A B S T R A C T

The use of polymers in tribology is continuously on the increase and technology is placing ever increasing performance demands. Polymers having good mechanical properties from cryogenic to high working temperature are needed for a variety of uses. As most of the polymers have low thermal stability, new polymers having high thermal stability are being synthesized and tried for high temperature tribological applications. From this point of view, the following polymers with chemical structures known for high thermal stability were chosen: Bismaleimides, Polyamideimide polyphenylene sulphide and phthalocyanines.

Bismaleimides are low molecular weight, thermosetting polymers. These can be synthesized by the reaction of diamine with maleic anhydride. On heating, these get polymerized without evolving volatile products resulting in a highly cross linked void free polyimides. The materials are a marked improvement over the condensation polyimides wherein water is produced during curing. The bismaleimides can be processed by the conventional techniques such as compressing and injection molding. Polyamideimide was second system chosen for the study. The polymer has both amide and imide groups. The amide linkages provide the necessary flexibility to the polymer backbone. This compound is thermally

stable and soluble in some solvents like DMSO, DMF. The third compound chosen was polyphenylene sulphide, which is known for its high thermal stability, good chemical resistance and easy processability. Sulphur atoms with lone pair of electrons give the polymer chain considerable stiffness due to which the polymer has a high m.p.(287°C). In air, at high temperatures, it undergoes crosslinking and chain extension reactions, darkens in colour and produces an infusible crosslinked polymer. The fourth type of compounds selected were copper phthalocyanines. This system is known for high thermal and thermo-oxidative stability. In this study the three phthalocyanines, monomeric copper phthalocyanine (Phthalocyanine blue), oligomeric and polymeric copper phthalocyanine, were examined.

All these polymers were synthesized in the laboratory and characterized by using elemental and IR analysis. Thermal and electrical properties of these polymers were also studied. The polymers showed remarkable thermal stability. Decomposition of bismaleimides started at 400°C and maximum weight loss occuring at 480°C. Polyamideimide registered 15% weight loss at 400°C, although it showed 5% weight loss between 100-150°C. Polyphenylene sulphide and phthalocyanines were more thermally stable and showed no weight loss upto 400°C.

With the exception of phthalocyanines, the polymers showed low conductivity (of the order of 10^{-14} to 10^{-16} ohm^{-1} cm^{-1}) and low values of dielectric constant. Phthalocyanines possessed high conductivities (10^{-9} - 10^{-8} $ohm^{-1}cm^{-1}$) and had high values of dielectric constant (50-500).

Tribological properties of these polymers were studied with a Plint Friction and Wear Machine. Molybdenum disulphide, graphite, and PTFE were used as solid lubricant additives. Commercially available polymers Kerimid (Phone-Poulenc) and Rayton (Phillips Petroleum Company) were also studied. Bismaleimides had high coefficients of friction and high rates of wear. Addition of graphite reduced the coefficient of friction and rate of wear. MoS_2 + Sb_2O_3 and PTFE gave better results, reducing friction and wear at low as well as at high loads. Kerimid showed better friction and wear characteristics as compared to 4,4' bismaleimido diphenyl methane (BM).

Composites of polyamideimide were made using Kerimid as binder and MoS_2, graphite and PTFE as additives. These composites had good friction and wear characteristics at low loads. However, at higher loads rates of wear were considerably high. In case of polyphenylene sulphide, the bulk polymer had high coefficients of friction (0.4 - 0.8) and high rates of wear. Its composites with MoS_2 - Sb_2O_3 and PTFE had low coefficients of friction (0.2 - 0.4) and lower rates of wear (10^{-7}-10^{-8}gm/m

The two composites PPS + Pbo + Graphite + PTFE and PPS + MoS_2 + Sb_2O_3 + PTFE, showed better friction and wear characteristics than the other composites. The coefficient of friction for these ranged from 0.15 - 0.3 and rate of wear was in the range of 10^{-7} gm/m. Composites of phthalocyanines were made using Kerimid and Polyphenylene sulphide as binder. The coefficient of friction (0.3 - 0.4) of composites of monomeric copper phthalocyanine was lower than that of Oligomeric and polymeric copper phthalocyanines. However, the latter had lower rates of wear over the load range applied. MoS_2 - Sb_2O_3 and PTFE helped in reducing the friction and wear. Composites of phthalocyanine with Kerimid as binder gave better results than the compos with PPS.

C O N T E N T S

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ABREVIATIONS

BM	4,4' Bismaleimido Diphenyl Methane
K	Kerimid
PAI	Polyamideimide
PPS	Polyphenylene Sulphide
CuPh	Copper Phthalocyanine
Oligo CuPh	Oligomeric Copper Phthalocyanine
Poly CuPh	Polymeric Copper Phthalocyanine
DMF	Dimethyl Formamide
NMP	N-methyl Pyrolidon
Et_3N	Triethylamine
Ac_20	Acetic Anhydride
ROW	Rate of Wear
DADM	Diaminodiphenyl Methane
NaAC	Sodium Acetate