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Multifunctional Lubricant Additives Derived from Natural Amino Acids and Methyl Oleate

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Novel multifunctional additives were synthesized from methyl oleate via thioglycolic acid addition followed by condensation with different amino acid methyl esters. Seven additives were synthesized and the structures of all the additives were fully characterized by mass, IR and NMR spectral studies. The tribological properties were evaluated using laboratory tribotests in biolubricant base oil, which suggest that all the prepared compounds act as antiwear and extreme pressure additives. Among the synthesized additives, heterocyclic containing compounds exhibited superior performance compared to others. Antioxidant properties evaluated using differential scanning calorimeter reveal that all the additives improved the oxidation stability of base oil with heterocyclic based additives exhibiting better performance compared to commercial antioxidant BHT. The synthesized amino acid-based derivatives have potential as biodegradable multifunctional additives in biolubricant formulations.

1. Introduction

Although small amounts of additives are being applied in base oils in lubricant formulations, their environmental issues have become a major concern recently.[1-3] The use of vegetable oils as platform chemicals for biolubricant synthesis has numerous advantages, including inherent biodegradability and limited toxicity. Vegetable oils rich in oleic acid are considered to be potential substitutes for mineral oil based lubricating oils and synthetic esters[4]. They possess superior viscosity index, lubricity characteristics, and high solubilizing power for additive molecules for preservation. In terms of additives used in lubricants, it is observed that common heavy metals and additives containing zinc are reported be toxic and hence[5] heavy metal-containing lubricants are not suitable for machines in food industries and in agriculture. For example, a recent challenge in lubricant chemistry has been to protect the global environment by developing zinc dialkyldithiophosphate (ZnDP) alternatives for engine oils. Although ZnDPs are multifunctional additives and have a reasonable cost, they generate ash and phosphorus oxide that poison the catalysts used for exhaust gas treatment[6] which results in air pollution. Besides the risk of environmental pollution caused by triboactive elements, another factor to be considered for environmental protection is the renewability of resources. The consumption of fossil resources increases the CO_2 concentration in air, resulting in the risk of abnormal weather. This is why managing renewable resources is of importance for the global environment. Biomass obtained from plants is a promising renewable resource because its major components are derived from CO_2 and water through photosynthesis.

Amino acids are essential components in living tissues. Proteins and peptides are derived from amino acids during biosynthesis in plants and animals. Therefore, amino acid derivatives are inherently safe chemicals and renewable resources. Structurally, amino acids have at least two functional groups; that is, carboxyl and amino groups, with relatively small molecular sizes. These functional

groups are beneficial for introducing a new moiety that can exhibit specific properties.[7-9] Various organic reactions that convert amino acids into corresponding products are well known. These reactions make amino acids versatile building blocks for the molecular design of multifunctional lubricant additives.[10-14] In this work we present a new concept for the synthesis of thioether based amino acid derivatives from methyl oleate using thiol-ene coupling followed by condensation reaction. Thiol-ene coupling reaction (TEC) has been extensively studied in the past and is now gaining a lot of attention with the development of the click-chemistry concept.[15, 16] Thiol-ene radical addition represents efficient method of introducing the sulfur atom into vegetable oil derivatives.[17-20] In this article, we describe the functionalization of methyl oleate with acid group involving the TEC, followed by condensation reaction of acid moiety with amine group of amino acid esters. The objective of the present work is the synthesis of new bio-based amino acid derivatives by TEC on vegetable oil fatty esters. The synthesized derivatives were evaluated as multifunctional additives in biolubricant base oil.

2. Experimental

2.1 Syntheses of additives

Methyl oleate, azobisisobutyronitrile (AIBN), hydroxybenzotriazole (HOBt) and 1-ethyl-3(3-dimethylaminopropyl) carbodimide hydrochloride (EDC.HCl) were purchased from Sigma–Aldrich (St. Louis, USA). Thioglycolic acid, glycine, alanine, leucine, isoleucine, histidine, tryptophan, phenyl alanine, thionyl chloride, 4-dimethylamino pyridine (DMAP) were purchased from SRL (Mumbai, India). Silica gel (60–120 mesh) for column chromatography was purchased from M/s Acme synthetic chemicals (Mumbai, India) and pre-coated TLC plates (silica gel 60 F254) were purchased from M/s Merck (Darmstadt, Germany). All the solvents were purchased from M/s SD Fine Chemicals (Mumbai, India) and were of the highest grade of purity.

Synthesis of 2-(18-methoxy-18-oxooctadecan-9-ylthio) acetic acid from methyl oleate (2)

Methyl oleate (1000 mg, 3.38 mmol) and AIBN (56.5mg, 0.338 mmol) were dissolved in 25 mL chloroform. Thioglycolic acid (730 L, 10.05 mmol) was added to the contents and the reaction mixture was refluxed for 24 hr. The progress of reaction was monitored with TLC. After almost complete conversion of the reaction as monitored by TLC, the reaction mixture was extracted with dichloromethane followed by water washing to remove excess thioglycolic acid after which the organic layer was dried over sodium sulphate. A yellowish viscous liquid was obtained after evaporation of solvent under vacuum. The crude product was purified by column chromatography (hexane/ethylacetate: 87/13 v/v) to obtain 2-(18-methoxy-18-oxooctadecan-9-ylthio) acetic acid (1210 mg; 92.5 % yield).

^{1}H NMR ($CDCl_3$, ppm): 0.88 (t, 3H, -CH_2-$C\underline{H}_3$); 1.24-1.42 (m, 22H-$C\underline{H}_2$-CH_3); 1.52-1.57 (m, 4H, -$C\underline{H}_2$-CH-S-); 1.6-1.65 (m, 2H, $C\underline{H}_2$-CH_2-CO-) 2.31 (t, 2H -CH_2-C=O), 2.77 (p, 1H, -$C\underline{H}$-S-CH_2-); 3.25 (s, 2H, -CH-S-$C\underline{H}_2$-CO); 3.65 (s, 3H, CH_3-O-C=O). **^{13}C NMR ($CDCl_3$, ppm):** 14.1 ($\underline{C}H_3$-CH_2-); 22-32.2 (-$\underline{C}H_2$-); 34 (-$\underline{C}H_2$-C=O); 46.5 (-CH-S); 51.4 ($\underline{C}H_3$O-C=O); 174.5 (-$\underline{C}OOCH_3$); 176 (-$\underline{C}$OOH). **IR (cm^{-1}, $CHCl_3$)**: 3380(OH), 2924, 1738, 1710, 1436, 1174. **MS** (ESI, m/z) $[M-H]^+$ 389.

Preparation of amino acid methyl ester

Amino acid (12.12 mmol) was taken in methanol (30 mL) at 0-5° C to which thionyl chloride (18.18 mmol) was added slowly over a period of 10 min. After complete addition, amino acid was completely dissolved and the mixture was stirred at reflux temperature under nitrogen atmosphere. After 12 h, the reaction mixture was cooled to 20° C and methanol was distilled and product was dried under vacuum.

Synthesis methyl 9 or 10-(2-(2-methoxy-2-oxoalkylamino)-2-oxoethylthio) octadecanoate

2-(18-Methoxy-18-oxooctadecan-9-ylthio) acetic acid (600 mg, 1.55 mmol) was dissolved in dichloromethane (25 mL), stirred at 0-5° C under nitrogen condition. HOBt (284.5 mg, 1.86 mmol) and EDC.HCl (357 mg, 1.86 mmol) were added and stirred for 10 min. Amino acid methyl ester (2.3 mmol) and DMAP (189 mg, 1.55 mmol) were added and the contents were stirred at 0-5° C for 10 min. After complete addition, the reaction mixture was stirred at room temperature for 12 h under nitrogen atmosphere and the progress of reaction was monitored with TLC. After maximum conversion, the reaction mixture was extracted with dichloromethane, washed with water and dried over anhydrous sodium sulphate and concentrated to obtain the crude product. The crude product was purified by column chromatography (hexane/ethylacetate: 92/8 v/v) to obtain the corresponding thioether based amino acid derivatives (yield range 78-82 %).

Methyl 10-(2-(2-methoxy-2-oxoethylamino)-2-oxoethylthio) octadecanoate (**3a**)

Quantities of substrates taken: thioether acid (600 mg), glycine methyl ester (204.5 mg), yield obtained 82 % (583 mg).

^{1}H NMR ($CDCl_3$, ppm): 0.88 (t, 3H, -CH_2-CH_3); 1.22-1.43 (m, 22H-CH_2-CH_3); 1.48-1.57 (m, 4H, -CH_2-CH-S-); 1.6-1.62 (m, 2H, CH_2-CH_2-CO-) 2.31 (t, 2H -CH_2-C=O), 2.66 (p, 1H, -CH-S-CH_2-); 3.26 (s, 2H, -CH-S-CH_2-CO); 3.67 (s, 3H, CH_3-O-C=O); 3.77 (s, 3H, CH_3O-). 4.08 (d, 2H, NH-CH_2-C=O); 7.4 (bs, 1H, -NH).

^{13}C NMR ($CDCl_3$, ppm): 14.2 (CH_3-CH_2-); 22-32.2 (-CH_2-); 34.2-34.8 (-CH_2-C=O); 46.2 (-CH-S-); 51.4 (CH_3O-C=O); 52.4 (CH_3O-C=O); 169.6 (-COONH); 169.9 (NH-CH-COOCH_3); 174.5 (-COOCH_3).

IR (cm^{-1}, $CHCl_3$): 3357(NH), 2924, 1741(C=O), 1664(NH-C=O), 1438, 1174.

MS (ESI, m/z) $[M+Na]^+$ 482.

Methyl 10-(2-(1-methoxy-1-oxopropan-2-ylamino)-2-oxoethylthio) octadecanoate (**3b**)

Quantities of substrates taken: thioether acid (600 mg), alanine methyl ester (237 mg), yield obtained 82 % (598 mg).

^{1}H NMR ($CDCl_3$, ppm): 0.88 (t, 3H, -CH_2-CH_3); 1.22-1.42 (m, 22H-CH_2-CH_3); 1.43 (d, 3H, -CH-CH_3); 1.48-1.57 (m, 4H, -CH_2-CH-S-); 1.6-1.64 (m, 2H, CH_2-CH_2-CO-) 2.3 (t, 2H -CH_2-C=O), 2.63 (p, 1H, -CH-S-CH_2-); 3.23 (s, 2H, -CH-S-CH_2-CO); 3.67 (s, 3H, CH_3-O-C=O); 3.76 (s, 3H, CH_3O-). 4.59 (m, 1H, NH-CH-C=O); 7.43 (d, 1H, -NH-CH-). **^{13}C NMR ($CDCl_3$, ppm):** 14.1 (CH_3-CH_2-); 18.3 (CH_3-CH-); 22.6-31.8 (-CH_2-); 34.-34.6 (-CH_2-C=O); 47.2 (-CH-S-); 48.2 (NH-CH-); 51.4 (CH_3O-C=O); 52.4 (CH_3O-C=O); 168.9 (-COONH); 172.9 (NH-CH-COOCH_3); 174.2 (-COOCH_3).

IR (cm^{-1}, $CHCl_3$): 3342 (NH), 2928, 1742(C=O), 1674(NH-C=O), 1456, 1165.

MS (ESI, m/z) $[M+Na]^+$ 496.

Methyl 10-(2-(1-methoxy-3-methyl-1-oxopentan-2-ylamino)-2-oxoethylthio) octadecanoate (**3c**)

Quantities of substrates taken: thioether acid (600 mg), isoleucine methyl ester (333.5 mg), yield obtained 81 % (645 mg).

^{1}H NMR ($CDCl_3$, ppm): 0.88 (t, 3H, -CH_2-CH_3); 0.94 (t, 3H, -CH-CH_3); 1.16-1.42 (m, 22H-CH_2-CH_3); 1.48-1.57 (m, 4H, -CH_2-CH-S-); 1.6-1.64 (m, 2H, CH_2-CH_2-CO-) 1.9-1.94 (m, 1H, CH_3-CH-CH_2-); 2.3 (t, 2H -CH_2-C=O), 2.65 (p, 1H, -CH-S-CH_2-); 3.24 (s, 2H, -CH-S-CH_2-CO); 3.67 (s, 3H, CH_3-O-C=O); 3.74 (s, 3H, CH_3O-). 4.57 (m, 1H, NH-CH-C=O); 7.41 (d, 1H, -NH-CH-).

^{13}C NMR ($CDCl_3$, ppm): 11.5 (CH_3-); 14.1 (CH_3-CH_2-); 15.5 (CH_3-CH-); 22.6-31.8 (-CH_2-); 34-34.6 (-CH_2-C=O); 46.4 (CH_3-CH-); 47.4 (-CH-S-); 51.4 (NH-CH-); 52.1 (CH_3O-C=O); 56.6 (CH_3O-C=O); 169.1 (-COONH); 171.9 (NH-CH-COOCH_3); 174.3 (-COOCH_3).

IR (cm^{-1}, $CHCl_3$): 3354 (NH), 2928, 1742(C=O), 1680(NH-C=O), 1463, 1172.

MS (ESI, m/z) $[M+Na]^+$ 538.

Methyl 10-(2-(1-methoxy-4-methyl-1-oxopentan-2-ylamino)-2-oxoethylthio) octadecanoate (**3d**)

Quantities of substrates taken: thioether acid (600 mg), leucine methyl ester (333.5 mg), yield obtained 80 % (636 mg).

^{1}H NMR ($CDCl_3$, ppm): 0.88 (t, 3H, -CH_2-CH_3); 0.95 (d, 6H, -CH-CH_3); 1.22-1.42 (m, 22H-CH_2-CH_3); 1.48-1.56 (m, 4H, -CH_2-CH-S-); 1.6-1.71 (m, 4H, CH_2-CH_2-CO-); 2.3 (t, 2H -CH_2-C=O), 2.64 (p, 1H, -CH-S-CH_2-); 3.24 (s, 2H, -CH-S-CH_2-CO); 3.67 (s, 3H, CH_3-O-C=O); 3.73 (s, 3H, CH_3O-). 4.61 (m, 1H, NH-CH-C=O); 7.25 (d, 1H, -NH-CH-). **^{13}C NMR ($CDCl_3$, ppm):** 14.1 (CH_3-CH_2-); 21.8-31.8 (-CH_2-); 34-34.5 (-CH_2-C=O); 41.4 (CH_3-CH-); 47.4 (-CH-S-); 50.8 (NH-CH-); 51.4 (CH_3O-C=O); 52.2 (CH_3O-C=O); 169 (-COONH); 173 (-COOCH_3).

IR (cm^{-1}, $CHCl_3$): 3319 (NH), 2927, 1743(C=O), 1675(NH-C=O), 1460, 1164.

MS (ESI, m/z) $[M+Na]^+$ 538.

Methyl 10-(2-(1-methoxy-1-oxo-3-phenylpropan-2-ylamino)-2-oxoethylthio) octadecanoate (**3e**)

Quantities of substrates taken: thioether acid (600 mg), phenylalanine methyl ester (411.5 mg), yield obtained 80 % (678 mg).

^{1}H NMR ($CDCl_3$, ppm): 0.88 (t, 3H, -CH_2-CH_3); 1.22-1.34 (m, 22H-CH_2-CH_3); 1.4-1.51 (m, 4H, -CH_2-CH-S-); 1.58-1.64 (m, 2H, CH_2-CH_2-CO-) 2.3 (t, 2H -CH_2-C=O), 2.53 (p, 1H, -CH-S-CH_2-);3.14 (m, 2H, -CH-CH_2-Ph); 3.19 (s, 2H, -CH-S-CH_2-CO); 3.67 (s, 3H, CH_3-O-C=O); 3.72 (s, 3H, CH_3O-). 4.84 (m, 1H, NH-CH-C=O); 7.13 (d, 1H, -NH-CH-); 7.23-7.32 (m, 5H).

^{13}C NMR ($CDCl_3$, ppm): 14.1 (CH_3-CH_2-); 22.6-31.8 (-CH_2-); 34.1-37.7 (-CH_2-C=O); 46.8 (-CH-S-); 53.3 (NH-CH-); 51.4 (CH_3O-

C=O); 52.3 ($\underline{C}H_3O$-C=O); 127.1-135.7 (C-Ph); 168.9 (-$\underline{C}$OONH); 171.6 (NH-CH-$\underline{C}OOCH_3$); 174.2 (-$\underline{C}OOCH_3$).

IR (cm^{-}1, $CHCl_3$): 3355 (NH), 2930, 1741(C=O), 1674(NH-C=O), 1456, 1178.

MS (ESI, m/z) $[M+H]^+$ 550.

Methyl 10-(2-(3-isoindol-1-yl)-1-methoxy-1-oxopropan-2-ylamino)-2-oxoethylthio) octadecanoate (**3f**)

Quantities of substrates taken: thioether acid (600 mg), tryptophan methyl ester (501 mg), yield obtained 79 % (718 mg).

^{1}H NMR ($CDCl_3$, ppm): 0.88 (t, 3H, -CH_2-C$\underline{H}_3$); 1.14-1.42 (m, 22H-C$\underline{H}_2$-CH_3); 1.56-1.58 (m, 4H, -C$\underline{H}_2$-CH-S-); 1.59-1.64 (m, 2H, C$\underline{H}_2$-CH_2-CO-) 2.31 (t, 2H -CH_2-C=O), 2.45 (p, 1H, -C$\underline{H}$-S-CH_2-); 3.18 (m, 2H, -CH-C$\underline{H}_2$-Im); 3.34 (s, 2H, -CH-S-C$\underline{H}_2$-CO); 3.67 (s, 3H, CH_3-O-C=O); 3.69 (s, 3H, CH_3O-). 4.9 (m, 1H, NH-C$\underline{H}$-C=O); 7.04 (s, 1H), 7.11(t, 1H), 7.19(t, 1H), 7.35(d, 1H), 7.41(d, 1H), 7.55(d, 1H), 8.2 (d, 1H, -NH-CH-).

^{13}C NMR ($CDCl_3$, ppm): 14.1 ($\underline{C}H_3$-CH_2-); 22.6-31.8 (-$\underline{C}H_2$-); 33.9-34.5 (-$\underline{C}H_2$-C=O); 46.8 (-CH-S-); 53.1 (NH-$\underline{C}$H-); 51.4 ($\underline{C}H_3O$-C=O); 52.3 ($\underline{C}H_3O$-C=O); 109.8, 111.2,118.5,119.6,122.2,122.6, 127.5 136.1, 169.1 (-$\underline{C}$OONH); 171.9 (NH-CH-$\underline{C}OOCH_3$); 174.4 (-$\underline{C}OOCH_3$).

IR (cm^{-}1, $CHCl_3$): 3344 (NH), 2929, 1741(C=O), 1658(NH-C=O), 1437, 1178.

MS (ESI, m/z) $[M+Na]^+$ 611.

Methyl 10-(2-(3-imidazol-2-yl)-1-methoxy-1-oxopropan-2-ylamino)-2-oxoethylthio) octadecanoate (**3g**)

Quantities of substrates taken: thioether acid (600 mg), histidine methyl ester (388.5 mg), yield obtained 78 % (650 mg).

^{1}H NMR ($CDCl_3$, ppm): 0.88 (t, 3H, -CH_2-C$\underline{H}_3$); 1.22-1.39 (m, 22H-C$\underline{H}_2$-CH_3); 1.44-1.56 (m, 4H, -C$\underline{H}_2$-CH-S-); 1.58-1.64 (m, 2H, C$\underline{H}_2$-CH_2-CO-) 2.3 (t, 2H -CH_2-C=O), 2.66 (p, 1H, -C$\underline{H}$-S-CH_2-); 3.12-3.18 (m, 2H, -CH-C$\underline{H}_2$-Im); 3.24 (s, 2H, -CH-S-C$\underline{H}_2$-CO); 3.67 (s, 3H, CH_3-O-C=O); 3.71 (s, 3H, CH_3O-). 4.83 (m, 1H, NH-C$\underline{H}$-C=O); 6.84 (s, 1H) 7.6 (d, 1H, -NH-CH-); 7.99 (m, 1H).

^{13}C NMR ($CDCl_3$, ppm): 14.1 ($\underline{C}H_3$-CH_2-); 22.6-31.8 (-$\underline{C}H_2$-); 33.9-34.4 (-$\underline{C}H_2$-C=O); 46.6 (-CH-S-); 52.5 (NH-$\underline{C}$H-); 51.4 ($\underline{C}H_3O$-C=O); 52.3 ($\underline{C}H_3O$-C=O); 116.1-134.9 (C-Im); 169.7 (-$\underline{C}$OONH); 171.6 (NH-CH-$\underline{C}OOCH_3$); 174.2 (-$\underline{C}OOCH_3$).

IR (cm^{-}1, $CHCl_3$): 3345 (NH), 2927, 1741(C=O), 1649(NH-C=O), 1437, 1178.

MS (ESI, m/z) $[M+H]^+$ 540.

2.2 Characterization

The ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian 300 and 75MHz, respectively and TMS was used as an internal standard. Mass spectra were recorded using electron spray ionization on Waters e2695 Seperators module (Waters, Milford, MA, USA) mass spectrometer. IR spectra were recorded in dichloromethane on a on a Perkin-Elmer Fourier Transform (FT-IR) Spectrum BX instrument (Model: Spectrum BX; Connecticut, USA).

For evaluating the additive properties, the base oil containing additives (both test compounds and the commercial additives) was prepared by mixing of the additives with base oil at 60°C with constant stirring for 15 minutes.

2.3 Tribological test

The tribological performance of the prepared additives was conducted on a Stanhope SETA four-ball tester. The antiwear of the base oil with and without additive was measured per ASTM D 4172 method under the following conditions: rotating speed, 1200 rpm: load, 40 kg; test duration, 60 min and temperature was 60 °C, which increased to 65-70 °C at the end of the 15 min run. Wear scar diameter of the three lower balls measured using an optical microscope with an accuracy of ±0.01 mm. Duplicate tests were performed with a new set of balls, and average wear scar diameter values were reported. The extreme pressure of base oil with and without additive was measured per IP 239 method under the following conditions: rotating speed, 1475 rpm; test duration, 60 sec and temperature, ambient. In extreme pressure tests, a series of tests conducted with increasing 10 kg load until the balls welded, and the load at which welded observed is the weld point. The analysis was carried out in duplicate and the average of two measurements is reported.

2.4 Surface Analysis

The surface analysis and elemental distributions of the worn surfaces were obtained using scanning electron microscopy (SEM). Carl Zeiss scanning electron microscope (model no EVO 18, Germany) coupled with energy dispersive X-ray (EDX) was used to investigate the surface analysis and composition of the entire tribofilm on the rubbed surface of steel balls. Before analysis, all samples were ultrasonically rinsed with hexane and petroleum ether for 10 min.

2.5 Oxidative stability test

Antioxidant actitivity of synthesized compounds was determined with differential scanning calorimeter (DSC) accoring to ASTM E 2009-08. DSC analyses were conducted on Q-100 thermal analyzer from TA Instruments under oxygen atmosphere. The DSC instrument was calibrated with pure indium, and an empty open aluminium pan was used to obtain the base line correction. A small amount of sample (typically 1.5-3.0 mg) was placed in open aluminium pans and oxygen flow was maintained at 50 mL/min. The cell temperature was raised to 250 °C, at a heating rate of 10 °C/min. The analysis was carried out in duplicate and the average of two measurements is reported.

3. Results and discussion

As the sulfur compounds[21, 22] and amino acids derivatives [23, 24] are known to have lubricity properties, the combination of both the compounds could result in novel multifunctional additives. In the present study, we report the synthesis and characterization of novel lubricant additives from amino acids and methyl oleate. The additives were subjected for evaluation of properties such as antioxidant, antiwear and extreme pressure properties in a biolubricant base fluid namely, epoxy jatropha fatty acid n-butyl esters (EJB).

Initially methyl oleate (**1**) was functionalised with thioglycolic acid by radical addition under thermal condition using AIBN as initiator to obtain the corresponding thioglycolic acid addition product (**2**) in 92.5 % yield as shown in Fig. 1. The structure of the obtained product was confirmed by NMR, IR and mass spectral data. The hydroxy band in IR at 3380 cm^{-1} was observed in the product. A strong band at 1738 cm^{-1}, a characteristic band for carboxylic acid was observed in the thioglycolic acid addition product which confirmed the formation of thioglycolic acid addition product. The formation of C-S bonds in the product could be detected by the expected peak at 600-700 cm^{-1} in the IR spectrum. ^{1}H NMR spectrum of purified product clearly showed the disappearance of the vinylic and allylic hydrogen signals at 5.35 and 2.00 ppm respectively. In addition to the disappearance of the vinyl and allylic proton signals and appearance of new peaks corresponding to hydrogen atoms α to the sulfur atoms in fatty acid chain at 2.77 ppm and 3.25 ppm corresponding to methylene group between sulphur and carboxylic acid group were also clearly visible which confirms the thioglycolic acid addition product. ^{13}C NMR of purified product confirmed that the expected reaction product was formed. The peaks between 120 and 135 ppm corresponding to double bond carbon atoms were not traceable. New peaks at 46.5 and 30.0 ppm for carbons α to the sulfur atom were detected. In addition, peaks at 174.5 ppm due to carbonyl carbons of ester and peak at 176 ppm indicated presence of free carboxylic acid group. The molecular ion at m/z 387 [M-1] was observed in negative mode of ESI analysis which confirms that expected product was formed.

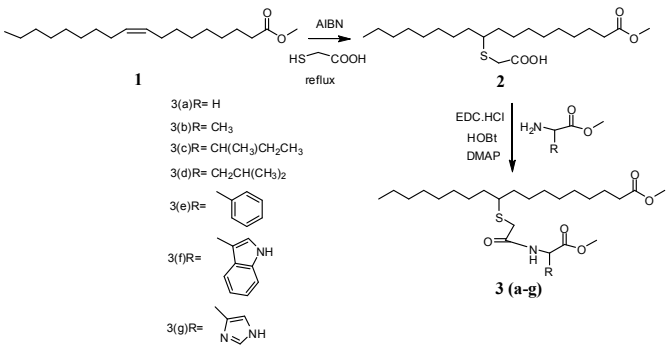


Fig.1 Synthesis of amino acid derivatives from methyl oleate

The thioglycolic acid addition product of methyl oleate was further coupled with seven different amino acid esters by condensation reaction to obtain the novel amino acid derivatives (**3a-g**) in yields ranging from 78-83 %. The structures of all the products were confirmed by IR, NMR and MS spectral data. IR spectra of all the derivatives showed a broad band at 3557 to 3319 cm^{-1} characteristic of -NH group. Carbonyl peaks corresponding to the both amide (~1650 cm^{-1}) and ester (~1740 cm^{-1}) functionalities further confirmed the formation of products. ^{1}H-NMR spectra of amino acid derivatives showed peaks at 7.4-8.0 ppm due to amide protons which indicated the amide formation. Singlet at 3.26 ppm indicates the protons of the methylene groups adjacent to the sulfur and carbonyl moiety. The aromatic protons are observed from 6.8 to 7.6 ppm for the aromatic amino acid derivatives like phenyl alanine, tryptophan and histidine. In ^{13}C NMR spectra peaks at 173 ppm due to carbonyl carbons of ester and peaks around at 170 ppm indicated presence of amide carbonyl carbon. Further, the mass spectral data showed the expected molecular weights for all the products which confirm the product structures.

3.1 Tribological Properties

Due to the presence of the sulfur and nitrogen atoms in the synthesised amino acid derivatives, the compounds can be projected as antiwear additives (AW). The AW properties of synthesized compounds at varying concentrations in base oil are shown in Fig. 2.

Fig. 2 depicts the comparative performance of antiwear characteristics of additives when blended in varying concentrations on a percentage weight basis in base oil. It can be seen that all the additives reduced the wear scar diameter (WSD) of base oil greatly. When the concentration of the additive was increased to 0.5% and above, the WSD was also increased and similar observations have been reported in the literature.[25, 26] This may be attributed to the formation of a more effective antiwear film by the additives through competing adsorption with base oil at a low concentration. It can be suggested that the synthesized compounds have better AW property at low concentration of 0.25%. The addition of commercial antiwear additive LZ1359 (commercial antiwear additive from Lubrizol Corporation) also improved the WSD of the base oil by 30%. The reduction in WSD was more for amino acid derivatives with tryptophan (**3f**) and histidine (**3g**), with a maximum reduction in the order of 25-27%. This could be due to the presence of heterocyclic indole and imidazole functional groups present in amino acids. This is attributed to the fact that the investigated additives are polar molecules with a number of active centers (indole and imidazole), which facilitate the adsorption of additive molecules on the steel surface. Among all amino acid derivatives, **3g** was found to exhibit excellent antiwear properties. Additives prepared from leucine and isoleucine exhibited similar performance as there is no difference in their molecular weight. Among the additives prepared from alanine and glycine, the alanine derivative exhibited slightly improved antiwear property compared to glycine. The reason for the improvement can be attributed to the additional CH_3 group present in alanine derivative in comparison to glycine derivative. The additional CH_3 group is capable of enhancing the antiwear behaviour as reported earlier[27, 28] and the same is observed in the present case. Additive derived from phenyl alanine showed poor antiwear performance, and one plausible explanation for this is due to the introduction of an aromatic ring in additive which causes fewer interactions between the phenyl group and base oil molecules, which tends to retard its antiwear behavior.[10]

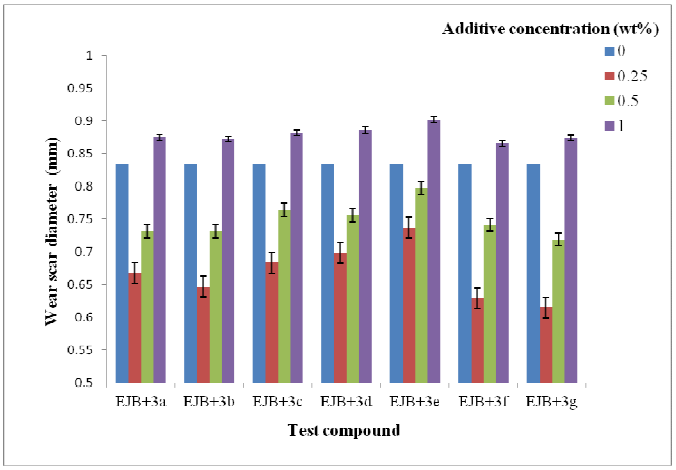


Fig. 2 Wear scar diameter of amino acid derivatives at different concentrations in EJB

The extreme pressure (EP) performance of both the base oil as such and base oil with additives at a concentration of 1% was evaluated. In general, the purpose of EP additives is to provide added wear protection and anti-seizing properties to both metallic surface and lubricant under higher loads and temperatures. Table. 1 presents the maximum weld load points of test samples containing the prepared derivatives, commercial EP additive, TCP (tricresyl phosphate) at 1.0 wt% and the control base oil without any additive. It can be observed that all the derivatives were greatly effective in enhancing the weld load. Specifically it was found that derivatives with heterocyclic amino acid derivatives (**3f, 3g**) exhibited the best performance compared to the other derivatives. These results suggest that the maximum weld loads of samples containing these derivatives have a positive correlation with the proportion of high hetero atom content with high weld load point. It has been reported that in the EP region, the surface layer is easily removed and a fresh metal surface is exposed continuously. Therefore, under these rigorous conditions, the additive that exhibits the best EP performance should be the one that reacts with the newly formed metal surface to generate the thickest protective film.[29] The additives containing S, O and N active EP elements[30] can react quickly with the metal surface to form a S-rich, O-rich and N-containing complex film, thus improving the EP property of base oil. Both these derivatives exhibited superior EP performance compared to TCP also.

Table 1: Extreme pressure activities of amino acids derivatives on epoxy jatropha fatty acid n-butyl esters (EJB) at 1% concentration

Test compound	Weld load (kg)
EJB	160
EJB +3a	200
EJB +3b	200
EJB +3c	200
EJB +3d	200
EJB +3e	210
EJB +3f	210
EJB +3g	220
EJB +TCP	200

3.2 Surface Studies

SEM analysis was carried out to examine the worn surface of the lower steel balls lubricated by base oil (EJB) and compared with base oil containing 0.25% of the prepared additive (3g). The SEM micrographs are presented in ×50 and ×500 magnifications in Fig. 3. The surfaces of base oil spiked with additive are smoother compared to the surfaces lubricated only with the base oil. It can be seen from Fig. (3A) that there are many deep furrows on the worn surface lubricated by base oil, which shows obvious signs of scuffing. This phenomenon suggests that the corresponding adsorption film was too weak to reduce the wear scar. Fig (3B) shows minor scratch under the same experimental condition. It is evident that smoothening of the surface occurred due to lower friction due to the presence of the additive, leading to formation of weak scars on the surface. In addition, the EDX spectrum of the wear scar in the presence of the additive and without additive is shown in Fig. 4. The EDX analysis shows the presence of nitrogen and sulfur on the worn surface of base oil containing additive (3g) which are due to the presence of additive in the base oil whereas these elements were absent in the EDX graph of base oil alone.

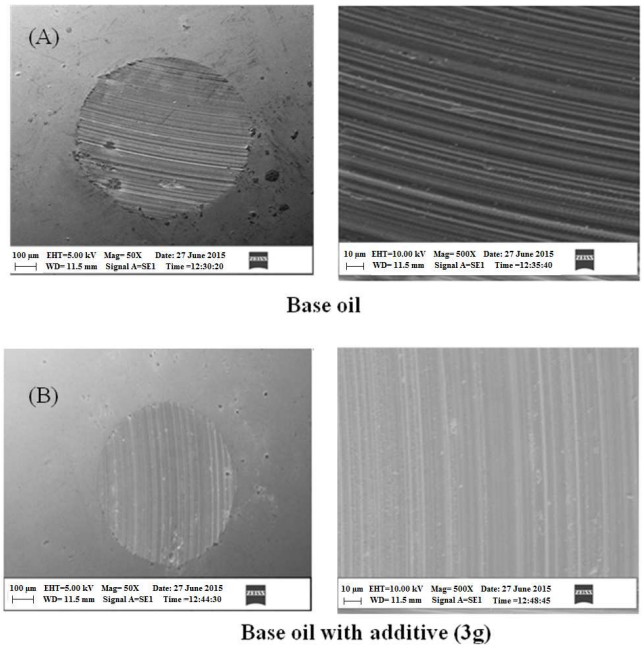


Fig.3: SEM morphologies of wear scar lubricated with base oil (A) and base oil containing 0.25% additive (3g)

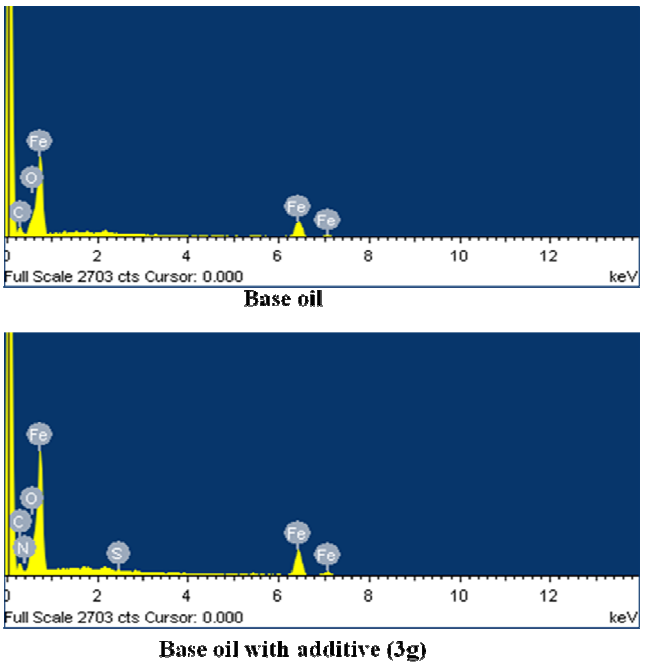


Fig. 4: EDX analysis data of the worn surface with base oil and base oil containing 0.25% additive (3g)

3.3 Antioxidant Property

Differential scanning calorimetry (DSC) was employed to understand antioxidant behaviour of the prepared additives in base oil, EJB and the results were compared with commercial antioxidant, BHT (butylated hydroxytoluene). DSC provides the onset

temperature (OT) and signal maximum (SM). They correspond to the temperatures when oxidation begins and maximum, respectively. Higher temperatures of onset and signal maximum are indications of higher oxidation stability of the tested samples.[31] The additive percentage in base oil was optimized using base oil doped with additive **3g** at 0.5, 1 and 2 % is shown in Fig. 5. Fig. 5 shows that when **3g** was added in incremental amounts of 0.5 and 1%, OT of the base oil (164.1) was also found to increase to 192.6 and 201.8°C respectively. This increase in oxidation stability was also observed on the SM values, where the base oil SM (198.4°C) increased to 226.6 and 242.2°C at 0.5 and 1% respectively. The maximum antioxidant activity was observed at 1 wt % concentration and when the additive dosage was increased to 2 % did not show any positive result. At 2% antioxidant concentration, the values of OOT and SM were observed to be 199.7 and 238.0 °C respectively. Hence, the antioxidant efficacy of synthesized amino acid derivatives and commercial antioxidant, BHT were evaluated at 1 wt % concentration in the base oil and the data is given in Table 2. From Table 2, it can be observed that all the derivatives are greatly effective in enhancing the OT and SM temperature of base oil. Hetero atoms (sulfur and nitrogen) containing compounds counter the alkyl hydro peroxides in the radical chain. The antioxidant molecule reacts with the peroxy radicals formed during oxidation and inhibit the radical propagating reaction forming more stable compounds. Moreover, sulphur and nitrogen-bearing compounds, especially the heterocyclic components are known to be effective antioxidants.[32] Among the all synthesized products amino acid derivatives with indole and imidazole groups exhibited the best performance and substantially higher antioxidant activity compared to BHT which can be observed in Table 2. The antioxidant performance of rest of the amino acid derivatives was similar. A typical dynamic DSC curve is given in Fig.6 showing dynamic curve of base oil without any additive and base oil with amino acid derivative (**3g**) and BHT at 1 wt % concentration in EJB base oil.

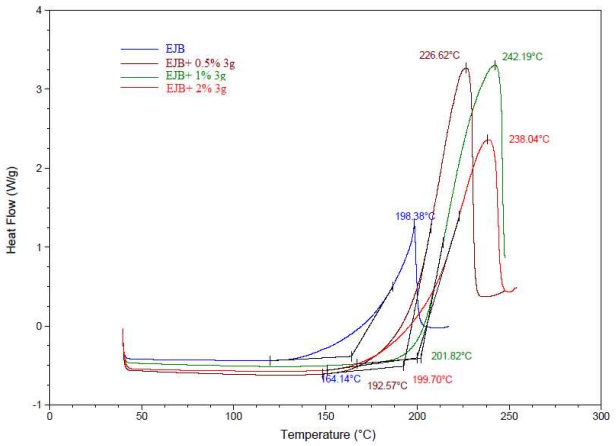


Fig.5: DSC curves for base oil with combination of **3g** with different concentrations.

Table 2: Antioxidant activities of amino acids derivatives on epoxy jatropha fatty acid n-butyl esters at 1% concentration

Test compound	**Onset Temperature** (°C)	**Signal Maximum** (°C)
EJB	164.1±0.05	198±0.4
EJB +3a	181.8±0.03	218.2±0.05
EJB +3b	181.5±0.06	218.1±0.08
EJB +3c	181.6±0.02	217.4±0.02
EJB +3d	184.4±0.04	218.8±0.03
EJB +3e	184.2±0.08	218.4±0.02
EJB +3f	196.8±0.05	232.6±0.02
EJB +3g	201.8±0.02	242.2±0.02
EJB +BHT	193±0.04	230±0.09

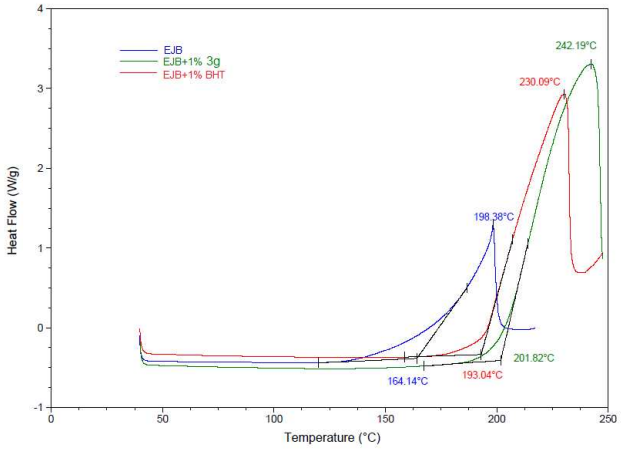
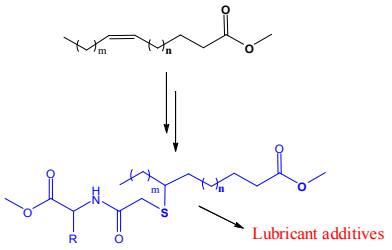


Fig.6: Antioxidant response of base oil with combination of **3g** and BHT using the DSC.

Inserting Graphics



Conclusions

Novel environmental friendly lubricant additives were synthesized from methyl oleate and natural amino acids and evaluated for tribological and antioxidant properties. The synthesized amino acid derivatives were found to exhibit antioxidant, extreme pressure and antiwear properties for the bio base oil. The tribological properties of the additives had a positive influence on the base oil, in particular additives with heterocyclics exhibited superior performance. All the additives improved the oxidation stability of base oil at 1% concentration and heterocyclic based additives exhibited better performance compared to reference antioxidant BHT. The synthesized products are promising candidates as novel multifunctional additives in biolubricant formulations.

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