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ORIGINAL ARTICLE

Synthesis and tribological investigation of 4-vinyl guaiacol–based thioether derivatives as multifunctional additives and their interactions with the tribo surface using quantum chemical calculations

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Abstract Novel 4-vinyl guaiacol based thioether derivatives were synthesized in a three-step reaction procedure by thiol-ene coupling as the key step. The synthesized compounds were characterised by spectroscopic techniques and evaluated for their tribological and antioxidant properties in two different base oils namely epoxy2-ethylhexyl esters of karanja fatty acids (EKE) and dioctyl sebacate (DOS). It was found that the synthesized products were exhibited superior antioxidant performance compared to butylated hydroxytoluene (BHT). All the three synthesized additives were improved the tribological properties of the base oil EKE and DOS. Dithio derivative at 0.75 wt % reduced the wear scar diameter by 36% and at 1 wt% improved the weld point by 33% of base oil EKE. Surface and elemental analysis result suggests that in the tribochemical process the synthesized thioether derivatives decompose and form an effective tribofilms on interacting surfaces. X-ray Photoelectron Spectroscopy (XPS) of the surface lubricated with base oil containing DMFD was evidence for the formation of tribofilm with FeS, $FeSO_4$ and Fe_2O_3. The antiwear behaviour of

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the additives was well correlated with quantum chemical calculations. Overall the dithio derivative is more effective as antiwear, extreme pressure and antioxidant bio lubricant additive than other thioether derivatives.

1. Introduction

The lubricant industry needs continuous efforts to develop new technological approaches to meet the requirements of modern industrial machines and automobiles in terms of saving energy loss and improving the efficiency of machinery [1,2]. Under this challenging scenario, there is a need for better lubricants components (base oil and additives) with minimal adverse effects on the environment. A conventional lubricant usually consists of 70–100% base oil and up to 30% chemical compounds called additives, which are utterly miscible. Additives are usually supplied in packages, in most cases the package contains a number of compounds that all have their own distinct functions. Such a package may, for example comprise friction modifiers, antiwear additives, extreme pressure agents, rust inhibitors, antioxidants, detergents and dispersants. These additives either impart new properties or improve the inherent properties of the lubricant. The demand for multifunctional additives (MFA) has been rising to minimize the number of additives in lubricant formulations. Conventional MFAs including zinc dialkyldithiophosphate (ZnDDP), molybdenum dithiocarbamate (MoDTC), additives composed with Cl, P, etc are not biodegradable and poisonous to the catalytic converter [3]. Although the additives are a minor portion of a lubricant, their toxicity cannot be neglected in order to make a lubricant ecofriendly. Therefore, the present trend in additive technology for lubricants focusing towards development of new additives with low toxic, ash less and bio degradable compounds [4-8]. Many reports have been published on the ecofriendly lubricant additives synthesized from fatty acids [9], amino acids [10], sugar [11] and polysaccharide [12] and explored as effective additives. The naturally occurring lipoic acid esters were synthesized and reported as multifunctional lubricant additives in high oleic sunflower oil and polyalphaolefin base oils [13]. Li et al., reported the use of natural garlic oil (NGO), an organosulfur compound extracted from cloves of garlic as a good environmentally friendly extreme pressure additive in PAO and synthetic polyol ester base oils [14].

Ferulic acid (FA) is a natural phenolic derivative of cinnamic acid present in plant cell walls [15]. It is a renewable feed stock for useful and value added chemicals such as guaiacol, vanillin, vanillic acid and protocatechuic acid [16,17]. Ferulic acid derivatives are well known bioactive molecules for their antiviral, anti tumour, antioxidant and antimicrobial activities [18]. Besides biological activity, FA derivatives are also potential molecules in various fields like cosmetics, food and surfactants. Thermal, chemical and biological degradation of FA gives 4-vinyl guaiacol (VG) [19-21]. VG has more chemical applications than FA due to its terminal double bond, which is more reactive towards radical reactions [22]. In the tribo chemical process the additives undergo decomposition to form protective tribofilms between interacting surfaces to minimise surface asperity [23]. Sulfur is one of the effective tribo active element and the tribo films formed with sulfur are relatively low hardness, shear strength and good adhesion to metal surfaces [24]. Therefore, sulfur containing compounds have been widely using as effective multifunctional lubricant additives as they can form protective tribofilms even at extreme conditions like high temperature and pressure [25-27]. In another study the combination of active elements such as sulfur-nitrogen, sulfur-oxygen and sulfur-sulfur additives were studied and reported as successful tribo active pairs [28]. Thioether derivatives are a class of organosulfur compounds which provide better antioxidant activity due to their peroxide decomposing function [29]. In recent, thiol-ene coupling (TEC) reactions has received considerable attention in development of new value added products for various applications in pharmaceutical, polymer and material science. TEC is a simple addition reaction between a thiol molecule and a double bond by thermal or light irradiation with high yields [30,31]. Along with hetero atoms, additives composed with long alkyl chains were exhibit advantages as efficient lubricating oil additives in the lubricant formulation. Addition of long-alkyl chain as a part of additive enhances the lipophilicity of additives to achieve excellent dispersion capability and stability in the lubricating oil [32]. Moreover, hydrophobic alkyl chains especially the long alkyl chain in the additive protect the metal surfaces due to its anti-rust ability [33]. Further, in view of the requirement for the development of new ecofriendly, biolubricant our team focused to synthesize multifunctional additives. Combined with the benefits of 4-vinyl guaiacol, fatty alkyl chain and thio ether, in the present manuscript, we report synthesis and characterization of three different 4-vinyl guaiacol based thioether additives for the first time and evaluation of their antioxidant, lubricity performance and lubrication mechanism by blending on two different lube oils. Their tribological properties were investigated by using four-ball tribotester and the surface topography, elemental composition on the worn metal surface was studied by scanning electron microscope (SEM) and X-ray photoelectron spectroscopy. The competing adsorption among the synthesized sulfur compounds on the metal surface has been achieved by the quantum chemical calculations using density functional theory (DFT).

2. Experimental

2.1. Materials

Ferulic acid (99%), myristoyl chloride (98%), 1,2-ethane dithiol (98%), 1,1′-azobis(cyclohexanecarbonitrile) (ABCN) (98%) 2-mercaptoethanol, cysteamine hydrochloride and sodium acetate were purchased from M/s Sigma Aldrich (St. Louis, USA). 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 Merck (Darmstadt, Germany).

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Highest grade purity of solvents were purchased from M/s SD Fine Chemicals (Mumbai, India).

2.2. Synthesis of 2-methoxy-4-vinylphenol (FDC)

Ferulic acid (1.0 g, 0.005 mol) and sodium acetate (0.21 g, 0.002 mol) were dissolved in dry DMF (20 mL) and refluxed at 130 °C for 1 h under nitrogen atmosphere and the progress of the reaction was monitored with TLC using the solvent system hexane and ethyl acetate (90:10,v/v). After completion of reaction contents were washed with water and ethyl acetate, the crude product was loaded on silica column running with hexane to get 80% yield (0.6 g) of the pure product. ^{1}H NMR ($CDCl_3$, ppm): δ 6.98–6.84 (m, 2H), 6.64 (dd, J = 18.1, 11.3 Hz, 1H), 5.64 (s, 1H), 5.59 (dd, J = 18.1 Hz, 1H), 5.13 (dd, J = 10.5 Hz, 1H), 3.92 (s, 3H, –OCH_3). ^{13}C NMR ($CDCl_3$, ppm): δ 149.14, 147.93, 136.12, 131.31, 122.90, 116.87, 114.36, 108.12, 56.14. MS (ESI, m/z):151 [M + H]$^+$.

2.3. Synthesis of 2-methoxy-4-vinylphenyl tetradecanoate (MFDC)

FDC (1.0 g, 0.006 mol), myristoyl chloride (3.27 g, 0.013 mol), triethyl amine (0.25 mL) were dissolved in dry DCM (15 mL). The reaction mixture was stirred at rt for 3 h and the product formation was monitored by TLC using solvent system hexane and ethyl acetate (90:10, v/v). After completion of reaction the crude reaction mixture was extracted in to ethyl acetate, washed with water and dried over anhydrous sodium sulphate. The crude product was purified by silica gel column using hexane/ethyl acetate (90:10, v/v) to get 83% yield (1.8 g) of the pure product. Mp 58–59 °C; ^{1}H NMR ($CDCl_3$, ppm): δ 6.96–6.82 (m, 2H), 6.63 (dd, J = 18.1, 11.3 Hz, 1H), 5.62 (s, 1H), 5.58 (d, J = 18.1 Hz, 1H), 5.09 (d, J = 10.5 Hz, 1H), 3.64 (s, 3H, –OCH_3), 2.56–2.54 (t, 2H,–CH_2CO), 1.67 (m, 2H, –CH_2), 1.40–1.32 (m, 4H, 2xCH_2), 1.28–1.26 (m, 16H, 8xCH_2), 0.88 (t, 3H, –CH_3). ^{13}C NMR ($CDCl_3$, ppm): δ 172.34, 151.12, 141.90, 136.17, 131.34, 122.95, 116.88, 114.32, 108.10, 56.14, 33.55, 31.97, 29.64, 29.35, 25.23, 22.74, 14.12. MS (ESI, m/z): 383 [M + Na]$^+$.

2.4. Synthesis of 4-(2-((2-aminoethyl)thio)ethyl)-2-methoxyphenyl tetra decanoate (MFDN)

MFDC (1.0 g, 0.0027 mol), 2-mercapto ethylamine hydrochloride (0.9 g, 0.008 mol) and ABCN (0.03 g, 3 wt% of MFDC) were dissolved in dry chloroform (15 mL). The reaction mixture was stirred at 85 °C for 16 h under nitrogen atmosphere. The formation of product was monitored by TLC using hexane and ethyl acetate (90:10, v/v). After completion of the reaction contents were washed with water and dried over anhydrous sodium sulphate. The crude product was loaded on silica gel column running with hexane/ethyl acetate (90:10, v/v) to get 85% yield (1 g) of the pure MFDN. Mp 74–75 °C; ^{1}H NMR ($CDCl_3$, ppm): δ 6.93–6.85 (m, 2H), 6.58 (dd, J = 18.1, 11.3 Hz, 1H), 3.62 (s, 3H, –OCH_3), 3.06 (t, 2H, –CH_2NH), 2.90 (t, 2H, Ar-CH_2), 2.77–2.73 (m, 4H, -SCH_2), 2.56 (t, 2H, –OCH_2), 1.65 (q, 2H, –CH_2), 1.33–1.30 (m, 4H, 2xCH_2), 1.31–1.25 (m, 16H, 8xCH_2), 0.88 (t, 3H, –CH_3). ^{13}C NMR ($CDCl_3$, ppm): δ 171.86, 153.22, 139.16, 137.31, 112.34, 61.57, 56.12, 40.41, 37.56, 33.58, 31.92, 29.63, 29.35, 25.23, 22.75, 14.14. IR (cm^{-1}, $CHCl_3$): 3379, 2924, 2853, 1760, 1511, 1151, 756. MS (ESI, m/z): 460 [M + Na]$^+$.

2.5. Synthesis of 4-(2-((2-hydroxyethyl)thio)ethyl)-2-methoxyphenyl tetra decanoate (MFDO)

Similarly, 4-(2-((2-hydroxyethyl)thio)ethyl)-2-methoxyphenyl tetradecanoate was synthesized from MFDC (1.0 g, 0.0027 mol), 2-mercapto ethanol (0.63 g, 0.008 mol) and ABCN (0.03 g, 3 wt% of MFDC) in 92% yield (1.1 g). Mp 78–79 °C; ^{1}H NMR ($CDCl_3$, ppm): δ 6.96–6.81 (m, 2H), 6.64 (dd, J = 18.1, 11.3 Hz, 1H), 3.68 (s, 3H, –OCH_3), 3.33 (t, 2H, –CH_2OH), 2.92 (t, 2H, Ar-CH_2), 2.74–2.70 (m, 4H, -SCH_2), 2.59 (t, 2H, –CH_2CO), 1.69 (m, 2H, –CH_2), 1.42–1.30 (m, 4H, 2xCH_2), 1.28–1.25 (m, 16H, 8xCH_2), 0.88 (t, 3H, CH_3). ^{13}C NMR ($CDCl_3$, ppm): δ 172.08, 151.27, 139.14, 138.44, 122.90, 112.69, 60.05, 56.32, 35.67, 34.28, 32.19, 30.01, 29.34, 24.77, 22.91, 14.10. IR (cm^{-1}, $CHCl_3$): 3422, 2924, 2853, 1761, 1465, 1150, 736. MS (ESI, m/z): 461 [M + Na]$^+$.

2.6. Synthesis of ((ethane-1,2-diylbis(sulfanediyl))bis(ethane-2,1-diyl))bis(2-methoxy-4,1-phenylene) ditetradecanoate (DMFD)

Similarly, ((ethane-1,2-diylbis(sulfanediyl))bis(ethane-2,1-diyl))bis(2-methoxy-4,1-phenylene) ditetradecanoate was synthesized from MFDC (1.0 g, 0.0027 mol), 1, 2-ethanedithiol (0.126 g, 0.0013 mol) and ABCN (0.06 g, 6 wt% of MFDC) in 75% yield (0.8 g). Mp 83–84 °C; ^{1}H NMR ($CDCl_3$, ppm): δ 6.90–6.88 (m, 4H), 6.59 (dd, J = 18.1, 11.3 Hz, 2H), 3.61 (s, 6H, 2x-OCH_3), 2.89–2.85 (t, 4H, Ar-CH_2), 2.82–2.78 (t, 4H, -SCH_2), 2.76–2.72 (t, 4H, -SCH_2SCH_2), 2.57 (t, 4H, –CH_2-CO), 1.64 (m, 4H, 2xCH_2), 1.42–1.30 (m, 8H, 4x-CH_2), 1.28–1.25 (m, 32H, 16x-CH_2), 0.88 (t, 6H, 2x-CH_3). ^{13}C NMR ($CDCl_3$, ppm): δ 173.50, 151.14, 139.68, 122.92, 120.63, 112.86, 56.06, 36.85, 33.65, 32.06, 30.12, 25.36, 23.06, 14.24. IR (cm^{-1}, $CHCl_3$): 2916, 2851, 1764, 1154, 718. MS (ESI, m/z): 837 [M + Na]$^+$.

2.7. Characterization

The synthesized compounds were characterized by ^{1}H and ^{13}C NMR spectra using TMS as internal standard on Varian 300 and 75 MHz, respectively. Waters e2695 separators module mass spectrometer was used to identify the mass, IR spectra were recorded on Perkin-Elmer Fourier transform (FT-IR) spectrum in chloroform solvent.

2.8. Physicochemical characteristics and lubricant properties

AOCS and ASTM standard methods were followed for the screening of tribology, copper strip corrosion, thermal and oxidation stability of synthesized products.

2.8.1. Tribological tests

The antiwear and extreme pressure properties of the synthesized additives in both base oils were examined by using

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four-ball tribo tester (Stanhope-Seta, UK) as per the method ASTMD 4172 and IP 239 respectively [31].

2.8.2. Surface characterization

The morphology of worn surface of three lower steel balls was analyzed by Carl Zeiss scanning electron microscope (SEM) (model no EVO18, Germany). The elemental composition of worn surface was investigated with energy dispersive X-ray spectroscopy (EDS) connected with SEM. The chemical state of elements present on worn metal surface was determined with a Kratos analytical Axis-Supra X-ray photoelectron spectroscope (XPS) instrument. Mg Kα X-ray was used as source and contaminated carbon (C1s: 284.8 eV) binding energy was taken as reference to calibrate the spectrometer.

2.8.3. Thermal stability

Thermal degradation temperature of synthesized additives was determined by thermo gravimetric analysis (TGA) using TA Q500 (TA Instruments, Inc., New Castle, DE, USA). Typically, 4–5 mg of sample was placed in α-Al_2O_3 crucible under continues nitrogen flow 60 mL/min at the heating rate of 10 °C/min from room temperature to 500 °C.

2.8.4. Oxidative stability test

Differential scanning calorimeter (DSC) was used to determine the oxidative onset temperature (OT) and signal maximum temperature (SM) as per the method ASTM E 2009–08 [31].

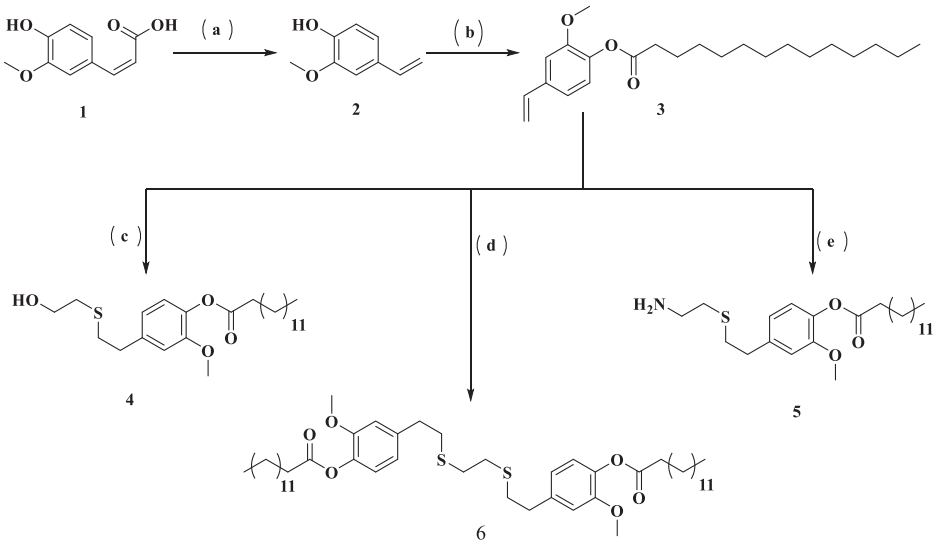
2.8.5. Theoretical studies

The electron density distribution at various centres of thioether derivatives was calculated by density functional theory (DFT) using B3LYP and fully optimized geometrical structures of all additives have been performed with the standard B3LYP/6-31G++(d,p) basic set using Gaussian 03, D.01 from the input of chemdraw structures [34].

3. Results and discussion

3.1. Synthesis and characterization

A new class of 4-vinyl guaiacol derivatives were synthesized as potential multi functional lubricating oil additives from ferulic acid in a three step reaction procedure as outlined in Scheme 1. In the initial step ferulic acid (1) was undergone decarboxylation by treating with sodium acetate in DMF to get 4-vinyl guaiacol (4-hydroxy,3-methoxystyrene) (2). In the subsequent step the derivate 3 was obtained by esterification of hydroxy group present on vinyl guaiacol (2) with myristoyl chloride. The terminal double bond present on derivative 3 was reacted with 2-mercaptoethanol, 2-mercapto ethylamine hydrochloride and 1,2-ethanedithiol in the presence of radical initiator ABCN under thermal conditions to get desired products (4–6) with good yields (75–92%). All the synthesized compounds were analysed in each step and the successful synthesis of target molecules was confirmed by NMR, ESI-MS and FT-IR spectral methods. In the ^{1}H NMR spectra the absence of signals at 5.09–5.62 ppm indicates the complete disappearance of unsaturation in all the three products (4–6). The triplet appeared at 2.72–2.77 ppm was corresponding to methylene protons α to the newly added sulfur atom and the peaks appeared at 2.85–2.92 ppm were due to β methylene protons of the sulfur atom. The characteristic peaks appeared at 2.56–2.59 ppm as a triplet adjacent to carbonyl group indicates the formation of ester and the peaks at 6.62–6.98 ppm were due to aromatic protons of phenyl ring. ^{13}C NMR spectra showed the signals at 31.92–32.06 ppm corresponding to carbons α to the sulfur atom. The aromatic carbon signals were



a) CH_3COONa, DMF, 1 h, 130 °C, b) $C_{13}H_{31}COCl$, N $(C_2H_5)_3$, DCM, rt, 4 h, c) 2- Mercaptoethanol, ABCN, $CHCl_3$, 80 °C, 16 h, d) 1,2-Ethanedithiol, ABCN, $CHCl_3$, 24 h, 80 °C, e) 2-Mercaptoethylamine hydrochloride, ABCN, 1,4- Dioxane,$CHCl_3$, 16 h, 80 °C. 4= MFDO, 5= MFDN, 6= DMFD

Scheme 1 Synthesis of 4-vinyl guaiacol based thioether derivatives.

observed at 112.34–151.27 ppm and the peaks appeared at 172.08–172.50 ppm correspond to the carbonyl carbon of ester group. The signals present at 14.10–36.85 ppm correspond to myristyl fatty chain carbons. In addition to NMR spectra FT-IR data also support the formation of the products. The signals appeared at 1760–1764, 1150–1154 cm^{-1} indicates the formation of ester and the prominent transmittance peak at 718–756 cm^{-1} due to the C-S bond clearly indicates the addition of sulfur atom. The characteristic peaks at 3422 cm^{-1} were due to hydroxy functionality of mercapto ethanol and in the case of amine derivative the characteristic peaks for amine group were observed at 3379, 1511 cm^{-1}. The signals appeared at ~ 2924 and ~ 2853 cm^{-1} were due to the -C–H (CH_2) stretching frequency of the fatty myristyl chain. Moreover, the formation of products was confirmed by molecular weights obtained from mass spectra in the form of molecular ions $[M + H]^+$, $[M + Na]^+$.

3.2. Thermal stability

Thermal analysis was performed to determine the thermal decomposition temperature of the additives. TGA curves were obtained by drawing a tangent between weight loss with corresponding temperature, the temperature at which the compound starts to lose its weight is called as thermal degradation temperature (T_d). Fig. 1 displays the T_d of additives ranging from 207 to 238 °C. Results showed that all the synthesized additives possess good thermal stability. Dithio derivative (DMFD) possessed excellent thermal stability with onset decomposition temperature at 238 °C whereas, MFDN and MFDO showed at 207, 208 °C respectively. The results justify that the synthesized additives with good thermal stability is suitable for their use as lubricant additives at higher temperature.

3.3. Antiwear performance

Four ball tribotester is one of the widely used tribo tester designed to examine the tribo performance of lubricant with high accuracy and reproducibility. A series of antiwear tests were conducted to evaluate the performance of synthesized compounds as effective antiwear additives in EKE and DOS base oils by increasing gradually concentration of additive, applied load and rotation speed. After completion of each test the wear scar obtained on test specimens were analysed and average scar diameter of test specimens was taken as mean wear scar diameter (MWD). Fig. 2 shows the effect of additive concentration on antiwear performance of base oils. From the figure the MWD of base oil decreased with increase in additive concentration from 0.25 to 0.75 wt%. At 0.75 wt% concentration all the three additives exhibited better antiwear efficacy compared to the neat base oils, it implies that the antiwear behaviour of the additive is dependent on its concentration [35]. Further increasing the additive concentration to 1.0 wt % resulted in larger MWD, which indicates that the additives demonstrated improved antiwear performance at a low concentration of 0.75 wt%. Above the optimum concentration (0.75 wt%) increase in wear scar diameter was observed. This could be due to the accumulation of a large amount of additive at the contact area leading to coagulation at the metal interface, which causes increase in friction force, tribofilm damage and severe wear [36].

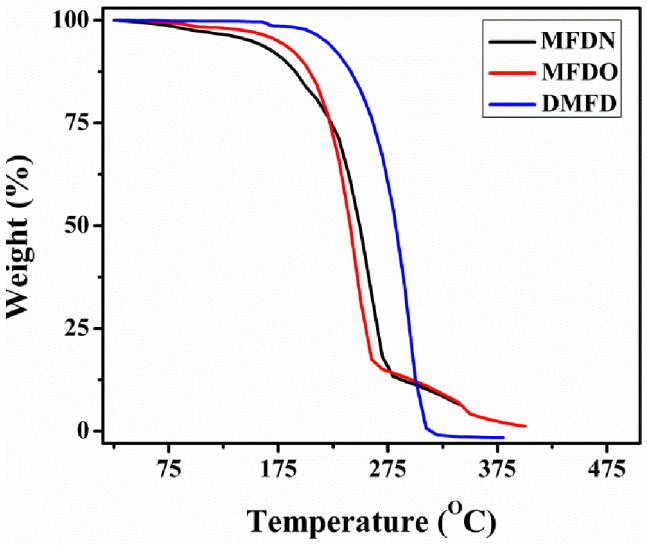


Fig. 1 TGA curves of 4-vinyl guaiacol based thioether derivatives under nitrogen atmosphere.

Fig. 2 shows that all the three additives respond well in both base oils and a significant change was observed in MWD. The additive DMFD (0.75 wt%) reduced the MWD of EKE from 0.842 to 0.546 and in the case of synthetic diester (DOS) it is from 0.872 mm to 0.562 mm. The effectiveness of synthesized additives was due to the formation of wear resistant tribofilms with sulfur. Sulfide films can protect the metallic surfaces from seizer by adhering to tribo-pairs [24,37]. Difference in antiwear performance was observed among the three additives clearly reveal that the MWD was dependent on type of hetero atoms present in additive. The maximum reduction in MWD was observed in the case of base oil blended with additive DMFD. Additive DMFD reduced the MWD of base oil by 36% whereas, commercial antiwear additive Lubrizol 1359 reduced the MWD of base oil by 38%. The antiwear behaviour of DMFD was slightly better than other additives may be due to the active-sulfur content present in the additive. Overall, order of antiwear efficacy followed as DMFD > MFDO > MFDN.

The wear scar diameter of neat base oil was high in the absence of additive at initial load (40 kg) and rotation speed (1200 rpm) however, MWD was increased by increasing the load from 40 to 80 kg. It was evident that at higher loads the interaction between metallic surfaces was more so the base oil failed to protect the surfaces. The effect of load on MWD of neat base oil and base oil blended with optimized concentration (0.75 wt%) of additives was studied by increasing the loads and the obtained results were shown in Fig. 3. It clearly illustrates that at the initial load (40 kg) MWD of the surface lubricated with two neat base oils was very high whereas, surface lubricated with additive blended base oils exhibited lower MWD. Further, increasing the load from 40 to 80 kg and recorded the MWD at each test, results observed that the MWD of surface lubricated with neat base oil was higher than the surface lubricated with additive treated base oils. Higher MWD observed by the surface lubricated with neat base oils and base oil blended additives at higher load may be due to decrease in the thickness of tribofilm between rubbing surfaces [38]. From the above discussion it can be con-

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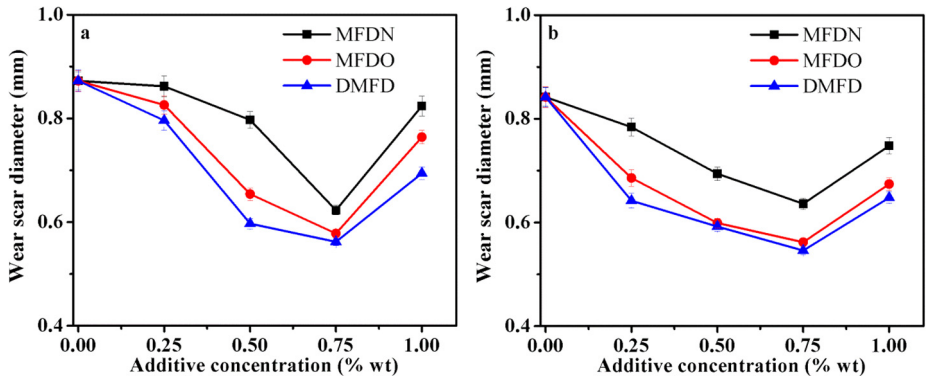

Fig. 2 Variation of wear scar diameter with different concentrations of additives in base oil (a) DOS, (b) EKE.

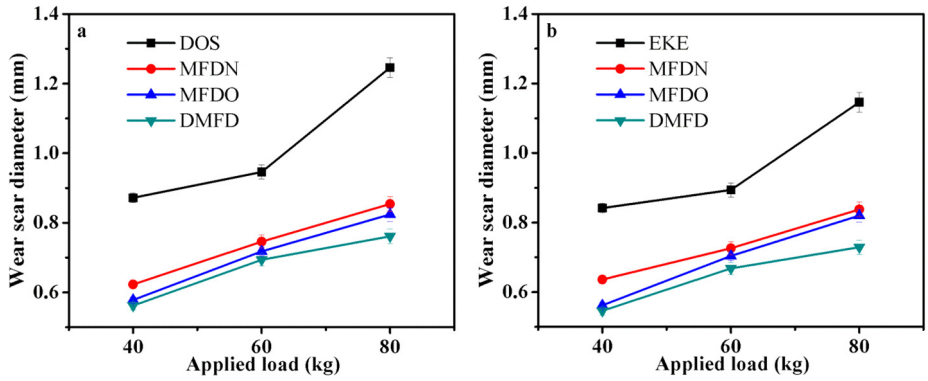

Fig. 3 Variation of wear scar diameter with different loads at 0.75 wt% of additive in base oil (a) DOS, (b) EKE.

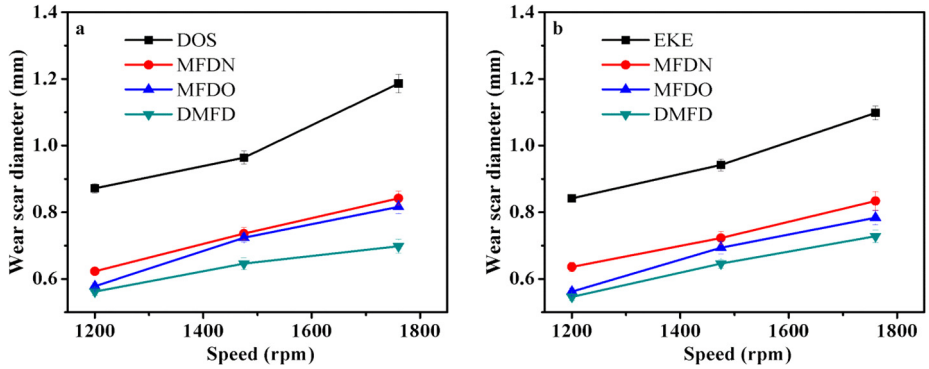

Fig. 4 Variation of wear scar diameter with different rotation speed (rpm) at 0.75 wt% of additive in base oil (a) DOS, (b) EKE.

cluded that the synthesized additives were potent antiwear molecules in both base oils even at higher loads.

Fig. 4 shows the variation of MWD with rotation speed of top ball on stationary lower balls. The effect of rotation speed on MWD was studied by varying the speed 1200, 1475 and 1742 rpm at fixed load (40 kg) and additive concentration at 0.75 wt%. The MWD was increased with increasing the rotation speed, at 1742 rpm there observed a higher MWD due to incomplete formation or less thickness of tribofilm [39]. Enzhu Hu et al., reported that by increasing the rotation speed an entrainment force is developed which results in oil film breakout [40]. Fig. 4 clearly indicates that all the additives have a positive impact in reducing MWD of base oil even at higher rotation speed.

3.4. Surface analysis

To get an insight into the mechanism of synthesized additives on the worn surfaces and elemental compositions of the worn surface was screened by using SEM, EDS and XPS spectra. Fig. 5 shows the photographs of the worn surfaces of balls lubricated with neat base oil EKE and EKE containing 0.75 wt% of the additives. The worn metal surface lubricated by the neat base oil exhibited a lot of furrowed wear tracks

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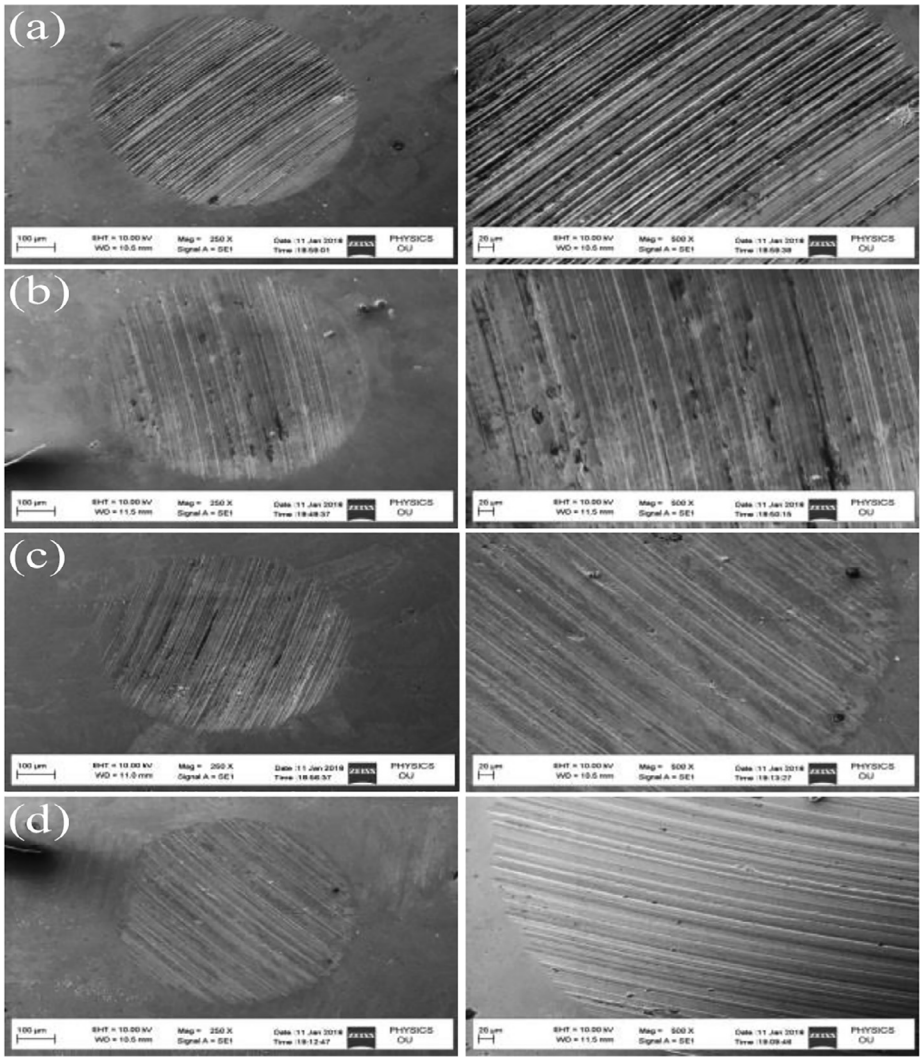

Fig. 5 SEM images of the worn surfaces lubricated with 0.75 wt% of synthesized additives in base oil (a) EKE, (b) MFDN, (c) MFDO, (d) DMFD.

and scratches (Fig. 5a) compared to the surface lubricated by the base oil containing synthesized additives (Fig. 5b-d). It clearly indicates that the interaction of the additive on metal surface decreased the deformation by creating an effective tribofilm. The result obtained from surface studies was further confirmed by EDS spectrum, which gives information about the elemental signals present on worn surfaces.

Fig. 6 shows the EDS spectrum of surface lubricated with base oil EKE and EKE blended with additives MFDN, MFDO and DMFD. It can be seen that the spectrum of surface lubricated with base oil blended MFDO and DMFD showed signals of sulfur atom and the spectrum of base oil doped with MFDN showed hetero atom nitrogen signal also whereas, these hetero atom signals were absent in the spectrum of surface lubricated with neat base oil. The element oxygen is common in all figures due to the formation of iron oxide. In addition to EDS spectra, elemental composition on the metal surface was also investigated by XPS analysis to derive further confirmation. Fig. 7 presents the XPS spectra of carbon, iron, sulfur and oxygen on the worn metal surface lubricated by 0.75 wt% of additive DMFD in base oil EKE. In O1s spectrum the peak at 532.2 eV could be attributed to $FeSO_4$ [41]. The prominent peak appeared at 711.3 eV in Fe_2p spectrum could be assigned to Fe_2O_3, Fe_3O_4 and $FeSO_4$ [41]. The two XPS peaks of S_2p observed at 161.5 and 168.8 eV correspond to FeS and $FeSO_4$ respectively [42]. The absence of particular Fe_2p peak of pure iron at 706.6 indicates that the interacting metal surface was covered by tribofilm [14]. The peaks exhibited by C1s at 285.4 and 287.2 eV correspond to –C(O)O– and C–C/C–H respectively indicate the presence of hydrocarbons [41]. The information drawn from the XPS analysis supports the formation of tribofilm by decomposition of additive on metal surface to form different chemical compositions by tribo chemical reactions.

3.5. Proposed antiwear mechanism

Antiwear tests shows that the synthesized thioether derivatives possess good antiwear performance in base oil by protecting the rubbing surfaces under severe experimental conditions. The surface and elemental analysis reports conclude that in the tribo-chemical process the thioether derivatives decom-

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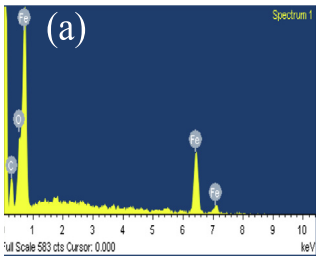
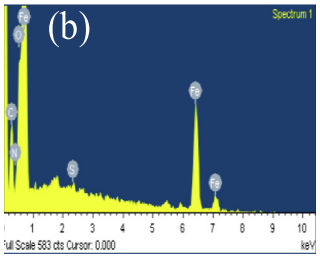
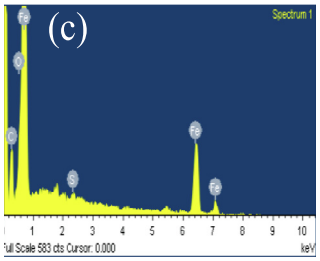


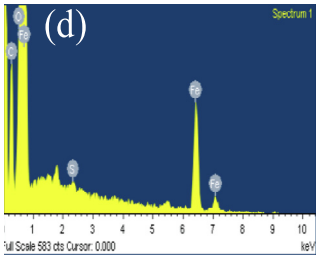
Element	Weight %	Atomic %
CK	8.88	28.16
OK	5.73	13.67
Fe L	85.39	58.17
Total	100	100



Element	Weight %	Atomic %
CK	9.73	26.22
OK	5.53	12.66
NK	0.99	2.58
SK	0.37	0.42
Fe L	83.38	58.12
Total	100	100



Element	Weight %	Atomic %
CK	8.93	30.04
OK	2.16	5.44
SK	0.35	0.44
Fe L	88.56	64.08
Total	100	100



Element	Weight %	Atomic %
CK	11.50	32.84
OK	8.24	17.68
SK	0.37	0.40
Fe L	79.89	49.08
Total	100	100

Fig. 6 EDS spectrum of the worn surfaces lubricated with 0.75 wt% of synthesized additives in base oil (a) EKE, (b) MFDN, (c) MFDO, (d) DMFD.

posed and adsorbed on metal surface through tribo active centers (S, N, O and phenyl ring). The presence of sulfur atoms in the synthesized additives can easily form FeS, which further generates FeS film on the metal surface. FeS film has high efficacy towards the metal surface due to its layered structure [43,44]. From the evidence of XPS and EDS spectra the protective films composed with FeS, $FeSO_4$, Fe_2O_3, and alkyl phenyl moieties could minimize the asperity between interacting surfaces to minimum wear. According to the above analysis the proposed antiwear mechanism of the base oil and base oil containing additives was shown in Fig. 8. Initially, there exist competitive adsorption between additives and base oil during the rubbing process [45]. The thioether derivatives dominantly adsorb on the metal surface since the polarity of thioether derivatives is higher than the base oil. Thereafter, the adsorbed additive decomposed under high pressure and high temperature to form adsorbed film and thereby reducing/minimizing wear whereas, high MWD observed with neat base oil may be due to the formation of broken tribofilm [46].

3.6. Quantum chemical calculations

Quantum chemical calculations were employed to explore the antiwear performance of synthesized additives and the effect of substituents on the basic skeleton. The full geometrically optimized structures of three synthesized additives MFDN, MFDO and DMFD were presented in Fig. 9. The data extracted from all the quantum chemical calculations like E_{HOMO}, E_{LUMO}, energy gap between HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) (ΔE), total energy and dipole moment (μ) were exhibited in Table 1. Physical or chemical adsorption of additive molecules on the metal surface is depending on polarity of additive and metal surface.

Frontier molecular orbital (FMO) approach is helpful to predict the strength of adsorption of additive molecule on the metal surface and also in prediction of chemical species reactivity. The energy gap between E_{HOMO} and E_{LUMO} is an index and it is responsible for the tribo chemical reactivity. Higher values of E_{HOMO} indicate the ease donation of electrons whereas, the lower values of E_{LUMO} indicates the acceptable ability of electrons. The effective adsorption is depend on ΔE, higher values of ΔE signifies the greater stability of additive molecule to interact with metal surface. Lower ΔE values containing additive adsorb greatly on metal surface in order to form an effective tribofilm. Huang et al., reported the calculations for energy of frontier molecular orbital of iron by considering iron as five-atom clusters [47]. The calculations of ΔE_1 (ΔE_1 = E_{LUMO} of iron-E_{HOMO} of additive) and ΔE_2 (ΔE_2 = -E_{LUMO} of additive-E_{HOMO} of iron) were employed to study the interaction between additives and iron. Electron transfer takes place from HOMO of additive (donor) molecule to the LUMO of iron ions (acceptor) [48,49]. Based on quantum chemical calculations among all the three thioether additives the smallest energy difference was observed between E_{HOMO} and E_{LUMO} of DMFD (Fig. 10). It was evident that the maximum interaction occurs with DMFD, thus DMFD acts as good antiwear additive among the three additives. The results drawn from the quantum chemical calculations were well correlated with the experimentally obtained wear results in the order of MFDN < MFDO < DMFD. Dipole moment (μ) is the measure of polarity of molecule and it is established when two equal magnitude containing electric charges of opposite signs are detached by a distance. Dipole moment is also one of the parameter to explain the antiwear behavior of additives. The dipole moments presented in Table 1 indicate that the additive DMFD possesses highest dipole moment and it exhibits the greater antiwear performance whereas, MFDN has lowest value of μ and its antiwear behaviour is also low. The data clearly implies that there is a good correlation between μ and antiwear behaviour.

3.7. Extreme pressure performance

The extreme pressure (EP) performance of synthesized additives was examined by conducting a series of EP tests by gradually increasing the load in 10 kg increment and noted the weld points. The base oils EKE and DOS showed weld points 160 and 120 kg respectively which was further enhanced to 240 and 190 kg when spiked with additive DMFD at 1 wt%. The effect of additive concentration was studied by varying addi-

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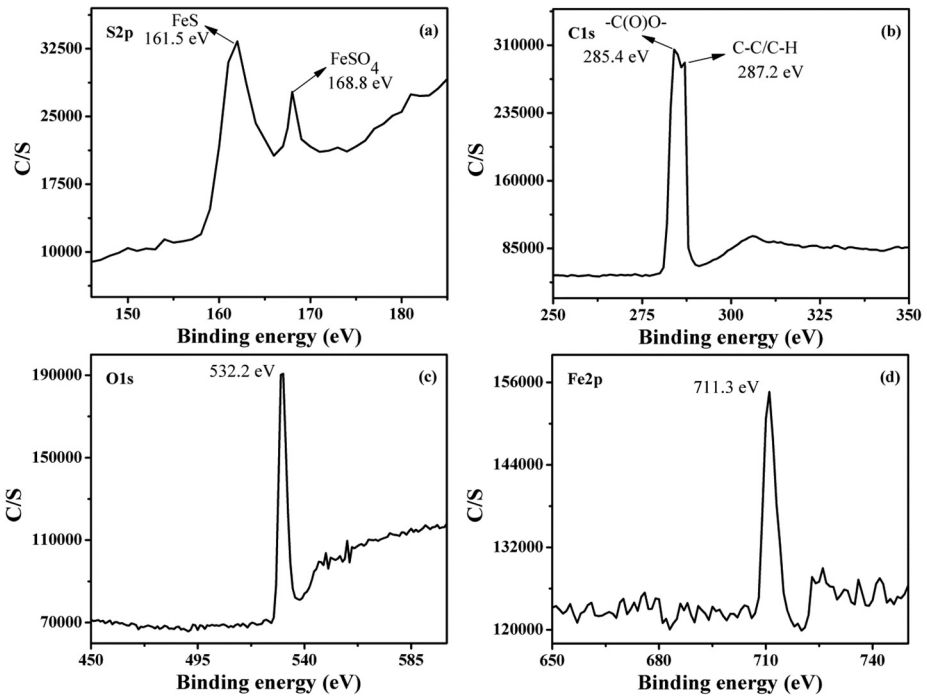

Fig. 7 XPS spectra of worn surfaces lubricated by 0.75 wt% of DMFD: (a) S2p, (b), C1s, (c) O1s and (d) Fe2p.

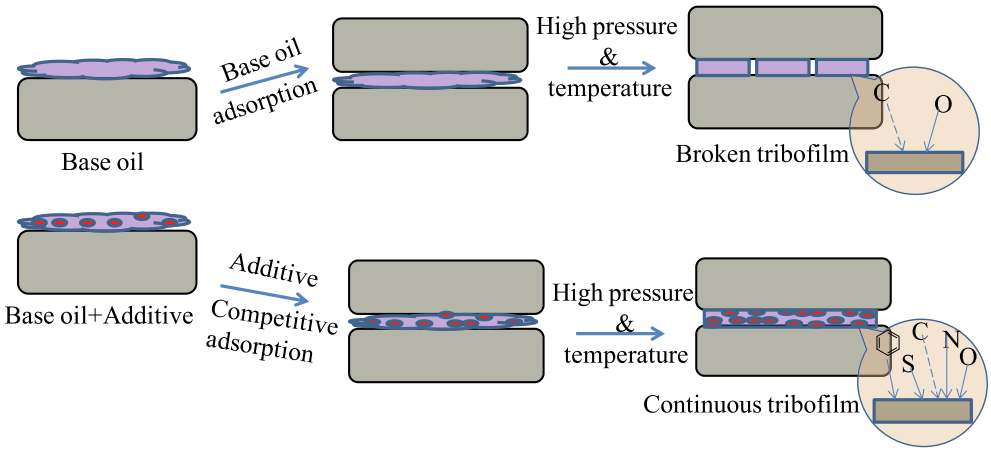

Fig. 8 Schematic diagram of the proposed antiwear mechanism of base oil and base oil containing additive.

tive concentration from 0.25 to 1.5 wt%. All the additive concentrations have resulted in higher weld points than neat base oil even at the low concentration of 0.25 wt%. While increase in concentration the load carrying capacity of the base oil increased up to 1 wt%. Further increase in the concentration did not show any improvement in weld point so 1 wt% was taken as optimum concentration. Fig. 11 indicates that all the synthesized additives exhibited good EP performance by improving the weld points of both base oils. The improvement in weld point clearly reveals that there was a significant action of additive. Improvement in weld point might be due to presence of tribo active elements of additives which contributes in the formation of a protective tribofilm between interacting surfaces [50]. The superior performance of additive DMFD may be due to the greater adsorption on metal surface by the formation of effective tribofilm through dithio moiety. Between the remaining two additives MFDN exhibited superior activity compared to MFDO, according to an earlier report the compounds with a combination of nitrogen and sulfur are good extreme pressure additives [51]. The weld points obtained with synthesized additives were compared with commercially available EP additive dibenzyl disulfide (DBDS), results indicate that the additives exhibited either comparable or better EP performance to commercial additive (Table 2).

3.8. Oxidative stability

DSC studies were conducted to evaluate the antioxidant performance of additives and the test results were compared with commercial antioxidant BHT (butylated hydroxytoluene). The

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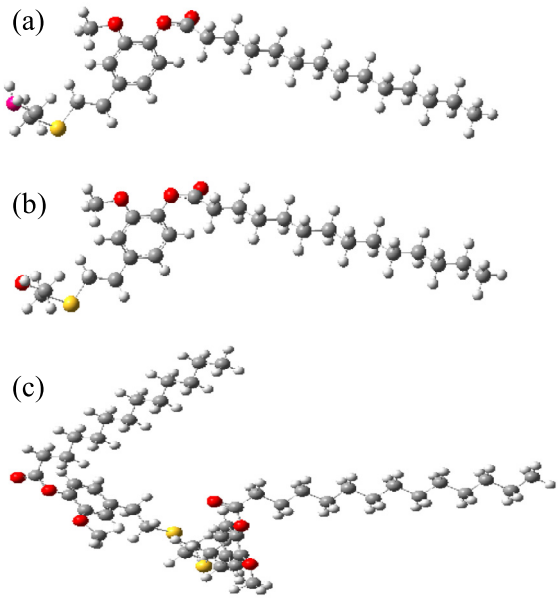

Fig. 9 Fully optimized geometrical structures of (a) MFDN, (b) MFDO, (c) DMFD (calculated with the B3LYP/6-31G + + (d, p) basis set).

onset temperature (OT) and signal maximum temperatures (SM) recorded from DSC explains about the efficacy of additive molecules as antioxidants. Higher temperatures of oxidation OT and SM are indications of higher the antioxidant efficacy of the tested compounds [52]. Additive concentration in base oil was optimized by adding DMFD in base oil DOS at three different concentrations. Neat base oil shown OT and SM at 180, 218 °C respectively and DMFD blended base oil exhibited OT at 211, 218, 216 °C at 0.5, 1.0 and 1.5 wt% concentration respectively. It indicates that 1 wt% was the optimum concentration so the antioxidant efficiency of synthesized additives and BHT were evaluated at 1 wt% additive concentration. Increase in OT and SM of both base oils was observed by the addition of additives (Table 3). All the synthesized additives exhibited superior performance compared to commercial antioxidant BHT in both base oils. The increased antioxidant activity of additives was due to the presence of thioether group, which provides better oxidation stability by peroxide decomposing function [29]. Additive DMFD exhibited superior performance compared to other two additives indicating negligent role of hydroxyl and amine functionalities in improving the oxidation stability of base oils.

Table 1 Calculated quantum chemical parameters of 4-vinyl guaiacol based thioether antiwear lubricant additives calculated by using B3LYP/6-31G + + (d, p) basis set.

Additive	Total energy (eV)	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE^a (eV)	ΔE_1^b (eV)	ΔE_2^c (eV)	Dipole moment (μ)
Fe_5 [47]		−5.074	−1.746	3.328			
MFDN	−45094.154	−5.750	−0.394	5.356	0.17203	0.14850	3.020
MFDO	−45634.653	−5.740	−0.398	5.342	0.17189	0.14711	3.579
DMFD	−83934.013	−5.788	−0.542	5.246	0.16660	0.14674	5.220

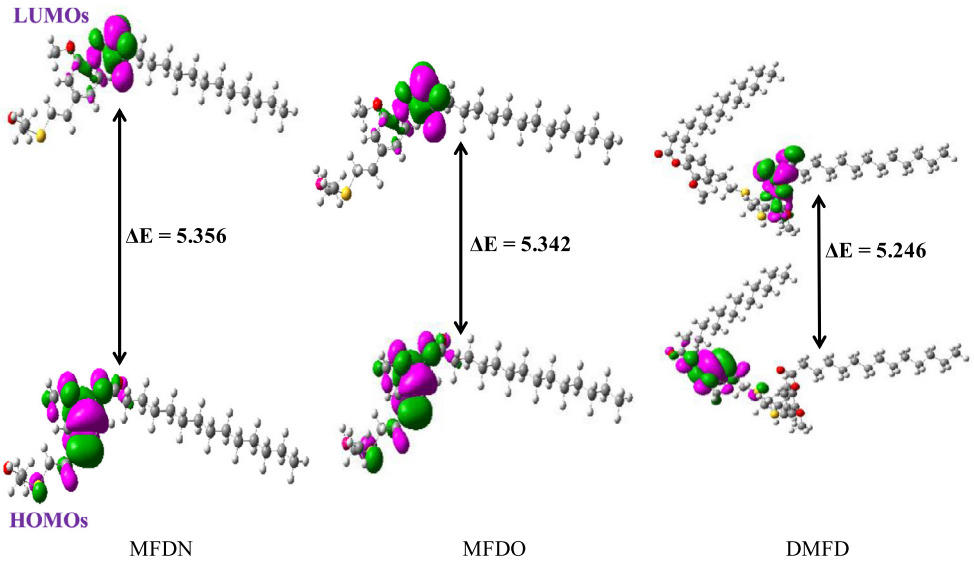

Fig. 10 Graphical representation of energy gaps between HOMO and LUMO density distributions of synthesized thioether derivatives.

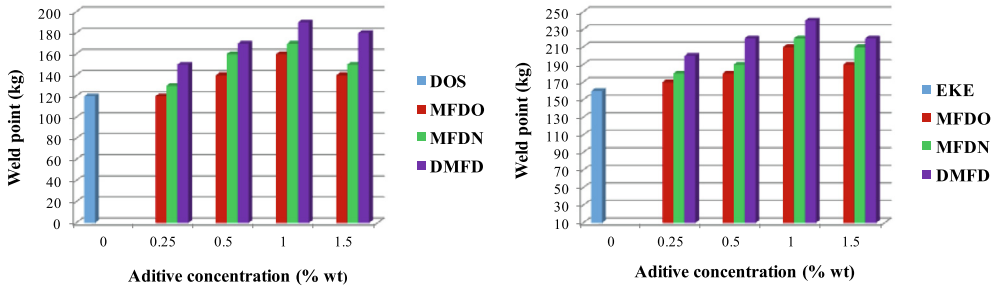

Fig. 11 Weld points at different concentration of additives in base oil DOS, EKE.

Table 2 Weld point of ferulic acid based thioether derivatives at 1 wt% concentration in both base oils.

Sample	Weld point (kg)	
	EKE	DOS
No additive	160	120
MFDO	210	170
MFDN	220	170
DMFD	240	190
DBDS	210	170

Table 3 Antioxidant activities of 4-vinyl guaiacol based thioether derivatives on both base oils at 1 wt% concentration.

Sample	EKE (°C)		DOS (°C)	
	OT	SM	OT	SM
No additive	166 ± 0.3	197 ± 0.7	180 ± 0.03	218 ± 0.06
MFDN	186 ± 0.08	215 ± 0.04	198 ± 0.06	238 ± 0.03
MFDO	188 ± 0.06	237 ± 0.05	199 ± 0.04	241 ± 0.04
DMFD	194 ± 0.4	240 ± 0.08	218 ± 0.08	289 ± 0.06
BHT	183 ± 0.09	217 ± 0.04	193 ± 0.04	230 ± 0.02

4. Conclusion

New 4-vinyl guaiacol based thioether derivatives were synthesized via thiol-ene addition reaction and characterized by NMR, mass and FTIR spectroscopy. Synthesized additives were analysed for tribological and antioxidant properties in DOS and EKE base oils. The synthesized compounds were found to have excellent extreme pressure and antiwear properties in both lubricant base oils. The maximum reduction in MWD of two base oils was observed at a lower additive concentration of 0.75 wt% at all rotation speed and loads. Among all the synthesized additives DMFD exhibited superior antiwear and EP performance. Surface studies conducted by SEM, EDS and XPS confirmed the development of tribofilm on the worn steel surface. XPS analysis of the surface lubricated with additive DMFD reveals that tribofilm consists of $FeSO_4$, FeS and Fe_2O_3 moieties. All the compounds exhibited maximum antioxidant activity at 1% concentration and found to be superior to commercial antioxidant. The synthesized additives were potential substitutes to toxic commercial additives for lubricant formulations.

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