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## Physicochemical and Tribological Properties of Triester Derivatives from Chemically Modified Waste Cooking Oil

<sup>1</sup>Shuo Xiang, <sup>1</sup>Ligong Chen, <sup>1</sup>Xin Yang, <sup>2</sup>Peili Zhang and <sup>3</sup>Liye Zhu

<sup>1</sup>Department of Military Oil Application and Management Engineering, Logistical Engineering University of PLA, Chongqing, 401311, People's Republic of China

<sup>2</sup>Chongqing Key Laboratory of Fire and Explosion Safety, Logistical Engineering University, Chongqing, 401311, China

<sup>3</sup>Oil Technical Supervision Office, Logistical Department of Chengdu Military Area, Chengdu, 610041, People's Republic of China

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#### Corresponding Author:

Ligong Chen,

Department of Military Oil Application and Management Engineering, Logistical Engineering University of PLA, Chongqing 401311, People's Republic of China

### ABSTRACT

Several triester derivatives with enhanced physicochemical and tribological properties were obtained from Waste Cooking Oil (WCO) through the following chemical modifications successively, transesterification of WCO, epoxidation of Fatty Acid Methyl Ester (FAME) and oxirane ring opening with anhydrides. Effect of the chain length increase of anhydrides on the low temperature fluid, viscometric properties and oxidation stability of triester derivatives were studied using pour point tester, viscometer and Pressurized Differential Scanning Calorimetry (PDSC), respectively. The tribological properties of triester derivatives were evaluated on a four-ball tribotester and the morphology of worn surfaces of steel balls was investigated by SEM. All triester derivatives showed better physicochemical properties, anti-wear ability and higher load-carrying capacity compared to 250BS, a representative of mineral oils. The three-step chemical modifications of the WCO re-utilization proposed in this study provide a feasible method to obtain high value-added and eco-friendly products, i.e., biolubricants.

**Key words:** Waste cooking oil, chemical modification, triester derivative, resource utilization, biolubricant

### INTRODUCTION

In recent years, the growing impetus for eco-friendly alternative lubricants has become a high priority in many countries which will play a large role in the industry and traffic in the near future. Conventional lubricants are based on mineral oils which have low biodegradability and high toxicity, resulting in that they are not environmentally friendly. A potential leakage of mineral oil based lubricants will create an environmental catastrophe, therefore any reduction or substitution is of great advantage (Kulkarni *et al.*, 2013). Waste Cooking Oil (WCO) is the byproducts of edible oils (such as canola oil, soybean oil, coconut oil, butter and fish oil) which differs across the world. In Chongqing municipality of China, the WCO comes mainly from hotpot and Sichuan

cuisine restaurants which is hard to dispose due to its high content of animal oils and complexity of the components (Gan *et al.*, 2009; Tu *et al.*, 2014). Waste minimization and reprocessing of WCO increasingly became a vital concern for governments and citizens.

As major components of WCO, animal and vegetable oils are promising alternatives to other synthetic and mineral-oil based lubricants due to their specific functional attributes such as high viscosity index, high lubricity, high flash point, very low volatility and biodegradability (Goud *et al.*, 2007; Hwang and Erhan, 2006). The WCO can be used to manufacture high value-added and eco-friendly products which otherwise finds no immediate potential way of resource utilization. It has been claimed that about 90% of the existing lubricant basestocks can be replaced by biolubricants

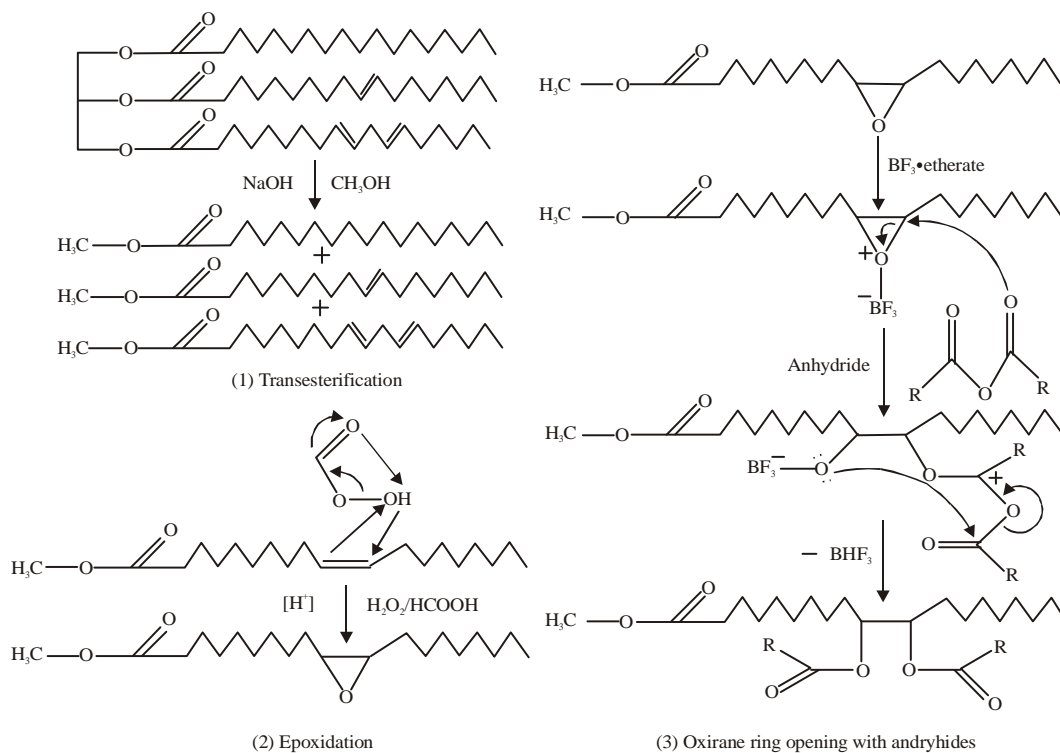


Fig. 1: Reaction scheme for the formation of triester derivatives. Triester derivatives: AWCO, when  $R=-CH_3$ ; PWCO, when  $R=-C_2H_5$ ; BWCO, when  $R=-n-C_3H_7$ ; i-BWCO, when  $R=-CH-(CH_3)_2$ ; HWCO, when  $R=-C_5H_{11}$

(Chowdhury *et al.*, 2013). However, WCO also has some disadvantages (such as poor low temperature fluid properties, susceptibility to oxidative degradation, propensity to undergo hydrolysis in acid media) which limit its application range (Moser and Erhan, 2007; Lathi and Mattiasson, 2007; Fox and Stachowiak, 2007). Therefore, it is necessary to modify the chemical structure of WCO, so that it can be used directly as lubricant basestocks. One potential way to improve the physicochemical and tribological properties of WCO is to attach some functional groups to the fatty acids, at their sites of unsaturation, through chemical modifications. Hydrogenation (King *et al.*, 2001), esterification (Sharma *et al.*, 2008), epoxidation (Carlson *et al.*, 1994; Campanella *et al.*, 2004; Findley *et al.*, 1945), metathesis (Holser *et al.*, 2006; Erhan *et al.*, 1997; Verkuijlen *et al.*, 1977), acylation (Sharma *et al.*, 2006), alkylation (Smith *et al.*, 2009; Smith *et al.*, 2010; Dailey *et al.*, 2009; Campanella *et al.*, 2010; Sharma *et al.*, 2007) or a combination of chemistries, have all been adopted in order to obtain an enhanced product.

In this study, a novel approach for WCO to prepare triester derivatives with enhanced physicochemical and tribological properties was proposed. Several triester derivatives were obtained through the following chemical modifications successively, transesterification of WCO, epoxidation of Fatty Acid Methyl Ester (FAME) and oxirane ring opening with anhydrides as shown in Fig. 1.

## MATERIALS AND METHODS

**Materials:** WCO was provided by a local hotpot restaurant with an acid value of 2 mg of KOH  $g^{-1}$ . Boron trifluoride diethyl etherate (98%), acetic anhydride (99.5%), propionic anhydride (98%), butyric anhydride (97.5%), isobutyric anhydride (97%), hexanoic anhydride (97%), methanol (99.5%), benzene (99.5%), formic acid (99.5%), hydrogen peroxide (30%) and methylene chloride (99.5%) were obtained from Aladdin Industrial Corporation, while sodium hydroxide, sodium chloride and sodium bicarbonate were of analytical grade and supplied by Chongqing Reagent Company and used as received without further purification.

### Methods

**NMR and FTIR:**  $^1H$  NMR spectra were recorded on Bruker (Boston, MA) Avance 500 NMR operated at 500.13 MHz using 5 mm broadband inverse Z-gradient probe in  $CDCl_3$  (Cambridge Isotope Laboratories andover, MA) and Bruker Icon NMR software was used. Each spectrum was Fourier-transformed, phase-corrected and integrated using MestRe-C 2.3a software (Magnetic Resonance Companion, Santiago de compostela, Spain). The FTIR spectra were recorded on a Shimadzu FTIR-8400 equipped with KBr beam splitter. Diffuse Reflectance System (DRS) was used for powder samples and NaCl plate for liquid samples by thin film deposition technique. A regular scanning range of 400-4000  $cm^{-1}$  was used for 45 repeated scans at a spectral resolution of 4  $cm^{-1}$ .

**Viscosity and viscosity index:** Glass capillary viscometer tubes were used to determine the kinetic viscosity of triester derivatives. Measurements were run in a constant temperature bath set at 40.0 and 100.0°C. Viscosity and viscosity index were calculated using GB/T 265-1988 and GB/T 19955-1988, respectively. Duplicate measurements were made and the average values were reported.

**Pour point (PP):** The pour points of triester derivatives were determined by following GB/T 3535-2006 at an accuracy of  $\pm 3^\circ\text{C}$ . The pour points were determined by placing a test jar with 50 mL of the sample into a cylinder submerged in a cooling medium. The sample temperature was measured in  $3^\circ\text{C}$  increments at the top of sample until the material stopped pouring. This point is determined when the material in the test jar did not flow when held in a horizontal position for 5 sec. The temperature of the cooling medium was chosen based on the expected pour point of the material. Test jars, thermometers, corks and rubber rings fully met GB/T 26985-2010 specifications. All runs were carried out at least in duplicate. Sample temperature was measured in  $5^\circ\text{C}$  increments at the top of the sample until it stopped pouring.

**Oxidation stability:** As a measure of oxidative stability, samples were subjected to PDSC analysis. The pressurized differential scanning calorimetry (PDSC) experiments were carried out using a PC-controlled DSC 2910 thermal analyzer from TA Instruments (New Castle, DE). A 1.5-2.0 mg of sample, resulting in a film thickness of less than 1 mm, was placed in a hermetically sealed type aluminum pan with a pinhole lid. This was oxidized in the presence of dry air which was pressurized in the module at a constant pressure of 1378.95 kPa (200 psi). Each experiment utilized a  $10^\circ\text{C min}^{-1}$  heating rate to get from 50-350°C. The oxidation onset (OT, °C) and signal maximum (SM, °C) temperatures were calculated from a plot of heat flow (W/g) versus temperature for each experiment. Each sample was run in triplicate and the reported average values with standard deviation.

**Friction and wear tests:** The anti-wear and friction-reducing properties of triester derivatives were evaluated using a four-ball friction and wear testers. Particularly, the maximum non-seizure load ( $P_B$ ) was tested with an MQ-800 four-ball friction and wear tester following the procedures of Chinese standard method GB/T 3142-92. Meanwhile, the Wear Scar Diameters (WSD) and friction coefficients were measured with an MMW-1P universal four-ball friction and wear tester. SAE 52100 steel balls with a diameter of 12.5 mm and a hardness of 59-61 HRC were adopted to assemble the frictional pair. Prior to friction and wear tests, the steel balls and specimen holders were cleaned in an ultrasonic bath with petroleum ether for 10 min and then dried with a hair dryer. After the friction and wear tests, the worn steel balls were rinsed ultrasonically with petroleum ether for 10 min and then used for surface analysis.

## Chemical modification

**Transesterification of WCO:** After the pretreatment of WCO, the transesterification reaction was carried out in a 500 mL three-necked glass flask connected with a reflux condenser, using tap water to condense the methanol vapor and a thermocouple probe. A 250 g aliquot of pretreated WCO was agitated at a constant stirring rate of 200 rpm and slowly heated from ambient temperature to  $60^\circ\text{C}$ , whereupon 2.5 g of NaOH dissolved in 50 g of  $\text{CH}_3\text{OH}$  was added into the pretreated WCO solution and the reaction was maintained at  $60^\circ\text{C}$  for 1 h. The mixture was left until a phase separation was observed, that is the FAME in the upper phase and glycerol in the bottom phase. The upper phase containing FAME was harvested and rinsed several times with de-ionized water until the color of the rinsed water was clear. Finally, the obtained FAME was vacuum dried at  $50^\circ\text{C}$  for 24 h.

**Epoxidation of FAME:** EFAME was prepared by reacting the FAME with performic acid generated *in situ*, at low temperature ( $20\text{-}40^\circ\text{C}$ ), using benzene as a diluent of the organic phase to lower viscosity and minimize ring opening. The chosen molar ratio of hydrogen peroxide/formic acid/double bonds of the FAME was 20/2/1. The FAME, benzene and formic acid were jointly placed into a 500 mL four-necked glass resin kettle equipped with mechanical stirrer with speed regulator, liquid addition funnel, thermometer pocket and energy regulator. After homogenizing the mixture for 30 min at  $70^\circ\text{C}$ , the predefined amount of 30% aqueous  $\text{H}_2\text{O}_2$  was placed in dropping cylinder and added over the period of 1 h. The reactor temperature was then slowly raised to  $40^\circ\text{C}$ , to complete the reaction ( $\approx 20$  h). The mixtures were next washed with distilled water until complete removal of performic and formic acids from the organic phase was achieved and then with NaCl (5 wt. %). Finally, water and benzene were separated from the epoxidized oils in a rotary evaporator.

**Oxirane ring opening with anhydrides:** Oxirane ring opening with anhydride reaction was carried out in a dry three-necked 500 mL round-bottom flask fitted with a condenser and a magnetic stirrer. A mixture of 50 g (0.16 mol) EFAME, 82 g (0.67 mol, 1:5 mol Eq.) acetic anhydride, 200 mL of methylene chloride and 2.5 g (17 mmol, 5 wt.%) boron trifluoride etherate as the catalyst was introduced into the flask. The reaction mixture was stirred and heated to the desired temperature, refluxing for 3 h under dry nitrogen atmosphere. After the reaction mixture cooled to room temperature, the product was purified by washing three times each with 100 mL of 5%  $\text{NaHCO}_3$  solution followed by 100 mL of brine solution. After cooling, an aliquot was treated with water and extracted with ether. The methylene chloride layer was dried over anhydrous magnesium sulfate (overnight) and filtered through a fritted funnel. The solvent was removed with rotary evaporation ( $\sim 60^\circ\text{C}$ , overnight) under reduced pressure and residual anhydride was removed by Kugelrohr evaporation under reduced pressure (0.2 torr vacuum) at  $70^\circ\text{C}$  to recover the triester derivative. The product (AWCO) was

then stored under vacuum. The above procedure was repeated using propionic, butyric, i-butyric, hexanoic anhydride for preparation of triester derivatives PWCO, BWCO, i-BWCO and HWCO, respectively.

## RESULTS AND DISCUSSION

**Characterization:** In the FTIR spectra of triester derivatives (AWCO, PWCO, BWCO, i-BWCO, HWCO), the absorption due to the C-O of epoxy group ( $822$  and  $842\text{ cm}^{-1}$ ) is not observed. This fact suggests that EFAME undergoes complete ring opening under the reaction condition. Formation of AWCO was also confirmed by the increase in peak intensity ratio  $1467:1375\text{ cm}^{-1}$ . In EFAME, the intensity of the  $1375\text{ cm}^{-1}$  peak is almost half-that of the  $1467\text{ cm}^{-1}$  peak, while in AWCO, due to addition of methyls ( $\text{COCH}_3$ ) in the structure, the peak at  $1375\text{ cm}^{-1}$  ( $\text{CH}_3$  bending vibrations) almost doubled compared to that at  $1467\text{ cm}^{-1}$  ( $\text{CH}_2$  bending vibration). Also the intensities of peaks such as  $1739\text{ cm}^{-1}$  (ester carbonyl) and  $1163\text{ cm}^{-1}$  (C-O stretching of esters) relative to that of the  $2930\text{ cm}^{-1}$  peak has increased in HWCO compared to EFAME. This is due to the increase in ester functionalities in the structure. A similar trend was observed in spectra of PWCO, BWCO, i-BWCO, HWCO, confirming the formation of the triester derivatives.

All triester derivatives were verified by  $^1\text{H}$  NMR spectroscopy in  $\text{CDCl}_3$ . The proton NMR peaks that are common in EFAME and triester derivatives are 2.2-2.5 ppm for  $\text{CH}_2$  protons  $\alpha$  to  $>\text{C}=\text{O}$ , 1.7-1.9 ppm for  $\text{CH}_2$  protons in between two epoxides, 1.6-1.7 ppm for  $\text{CH}_2$  protons  $\beta$  to  $>\text{C}=\text{O}$ , 1.2-1.6 ppm for other  $\text{CH}_2$  protons and 0.8-1.0 ppm for terminal  $\text{CH}_3$  protons. The number of protons shown for each product is computed using a reference value of four protons for peaks at 4.1-4.4 ppm corresponding to four  $\text{CH}_2$  protons of  $-\text{CH}_2\text{CHCH}_2-$  in the carbon chain of triester structure. It can be seen that intensity of peaks at 3.2-3.8 ppm due to the epoxy group decreased in all the triesters. All the triester derivatives have new peaks at 4.8-5.4 ppm in their  $^1\text{H}$  NMR spectra due to CH protons at the branching site ( $-\text{CHOCOR}$ ) on fatty acid chain. The presence of additional peaks at 1.83-2.2 ppm due to methyl protons of the  $-\text{COCH}_3$  group in  $^1\text{H}$  NMR spectra confirms the formation of AWCO. The formations of other triester derivatives could be confirmed in the similar way.

**Viscomeric properties:** Detailed knowledge of the viscometric property of triester derivatives is of particular importance whenever lubrication is their intended usage. The viscosity of triester derivatives compared to mineral oil 250BS is shown in Table 1. Viscosities of the prepared triester derivatives are higher than that of mineral oil 250BS. Their values vary in the range between 2.55 and  $10.44\text{ mm}^2\text{ sec}^{-1}$  at  $40^\circ\text{C}$  and the viscosity index between 109 and 135. The viscosity and viscosity index triester derivatives increased with the chain length increase of anhydrides which resulted from their higher molar weight and especially the altered structure of their molecules. The values of viscosity index are high, characteristic for oils of ester type.

Table 1: Effect of the chain length increase of anhydrides on the kinematic viscosity, viscosity index and pour point of triester derivatives

Lubricating oil	Kinematic viscosity ( $\text{mm}^2\text{ sec}^{-1}$ )		Viscosity index	Pour point (PP) ( $^\circ\text{C}$ )
	$40^\circ\text{C}$	$100^\circ\text{C}$		
FAME	5.02	1.87	-	-1
EFAME	8.81	2.55	122	0
AWCO	9.53	2.62	109	-3
PWCO	9.58	2.66	115	-9
BWCO	9.64	2.71	123	-15
i-BWCO	9.61	2.70	123	-17
HWCO	10.44	2.91	135	-20
250BS	1540	58.30	84	-7

**Low temperature fluid properties:** The pour point plays significant role in evaluation of low temperature fluid properties of the lubricants. Pour point values for FAME, EFAME, AWCO, PWCO, BWCO, i-BWCO and HWCO are given in Table 1. The pour point of FAME is  $-1^\circ\text{C}$ , while that of EFAME is  $0^\circ\text{C}$ . The triester derivatives are characterized by lower pour points as demonstrated by the superior pour points for HWCO ( $-20^\circ\text{C}$ ). The pour points decreased with the chain length increase of anhydrides. This can be rationalized by the presence of alkoxy groups attached at the site of unsaturation which does not allow for individual molecules to come close for easy stacking because of steric interactions and thus inhibiting crystallization, resulting in a lower pour point. The alkoxy groups of optimum length at the epoxy carbons not only serve to eliminate the sites of unsaturation but also impose spacing from other molecules, thereby interfering with the formation of macro-crystalline structures. The alkoxy groups with a chain length of six carbons were found to be the most effective for imposing the desired molecular spacing and thus imparting the most desired pour point properties.

**Oxidation stability:** The PDSC test is widely used in the lubricant industry for measuring oxidative stability of base oils as well as finished lubricants. The onset temperature of oxidation (OT) is the temperature when a rapid increase in the rate of oxidation is observed in the system. The signal maximum temperature of oxidation (SM) is the temperature at which maximum heat was evolved during oxidative degradation of the sample. The PDSC results, OT and SM, for triester samples are shown in Fig. 2 (Note: OT and SM values are the average of three experiments with a standard error of  $\pm 1^\circ\text{C}$ ). The triester derivatives showed higher oxidation stability than unmodified FAME and EFAME as shown by their higher OT and SM values. This increase in oxidation stability is due to the removal of unsaturation. With the chain length increase of anhydrides, no significant change was observed to the oxidation stability.

**Tribological properties:** An important property of lubricants is their ability to maintain a stable lubricating film at the metal contact zone. Ester oils are known to provide excellent lubricity because of their ester functionality. To further elucidate the effect of the chain length increase of anhydrides on the tribological properties, the extreme pressure properties,

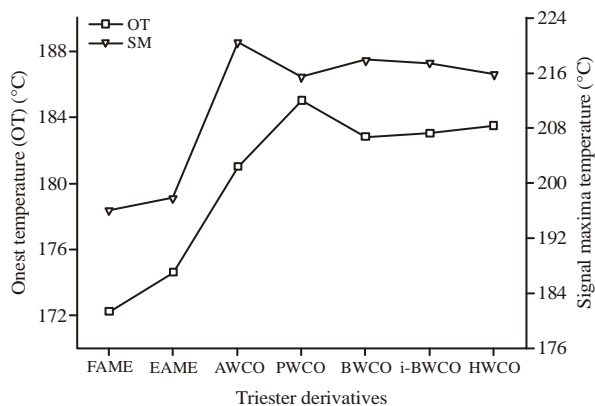


Fig. 2: Effect of the chain length increase of anhydrides on OT and SM. OT: Onset temperature of triester derivatives, SM: Signal maxima temperature of triester derivatives

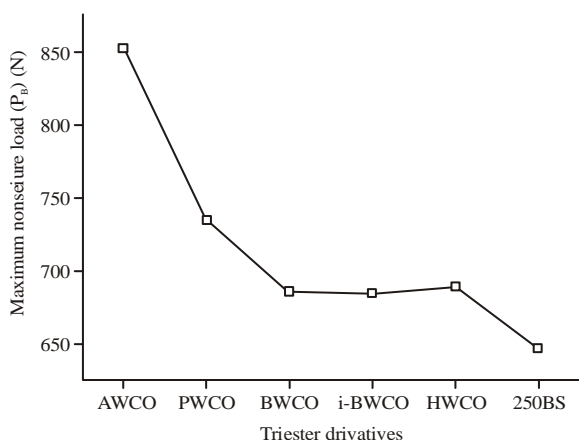


Fig. 3: Effect of the chain length increase of anhydrides on P<sub>B</sub> of steel ball. P<sub>B</sub>: Maximum nonseizure load of steel ball lubricated by triester derivatives and 250BS under conditions: speed, 1450 rpm; room temperature; time, 10 sec

the friction-reduction and anti-wear properties of triester derivatives (AWCO, PWCO, BWCO, i-BWCO, HWCO) were measured using a four-ball tribometer.

Under the conditions (speed of 1450 rpm, at room temperature for 10 sec), the extreme pressure properties of triester derivatives were demonstrated by the maximum nonseizure load (P<sub>B</sub>) obtained using an MQ-800 four-ball friction and wear tester according to GB/T 3142-1982. Figure 3 shows the effect of the chain length increase of anhydrides on the maximum nonseizure load (P<sub>B</sub>) of triester derivatives and mineral oil 250BS. The maximum nonseizure load of triester derivatives was 862.4 N, surpassed that of mineral oil 250BS. The P<sub>B</sub> value decreased with the chain length increase of anhydrides, because of the reduction of oxygen content in triester derivatives resulted in the decrease of affinity for metal surface.

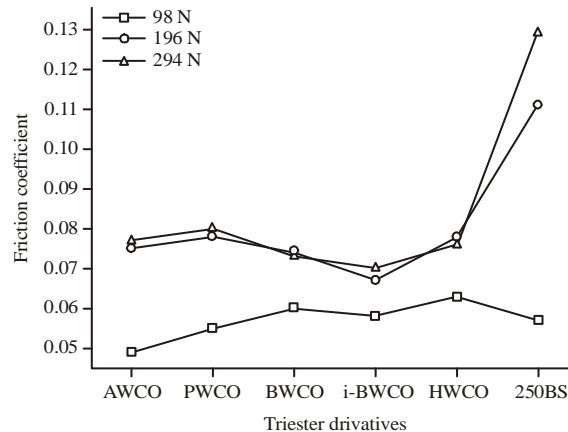


Fig. 4: Effect of the chain length increase of anhydrides on friction coefficient of steel ball. The steel ball was lubricated by triester derivatives and 250BS under conditions: varying load, from 98 N to 294 N; speed, 1200 rpm; room temperature; time, 30 min

Under the conditions (varying load (from 98-294 N), speed of 1200 rpm, at room temperature for 30 min), the friction-reduction properties of triester derivatives and mineral oil 250BS were demonstrated by the friction coefficient as shown in Fig. 4. The friction coefficient values of all triester derivatives are a considerable improvement over mineral oil 250BS. This shows that triester derivatives can be used as alternatives to mineral-oil based lubricants. The friction coefficient value decreased first and then increased with the chain length increase of anhydrides. The measurement of friction coefficient with increasing load helped determine the safe limits of load under which these triester derivatives can be used. Any further increase in load beyond a certain point would result in a catastrophic rise in friction coefficient value, primarily, because of irreversible breakdown of film and, second, because of the loss of oil-induced lubricating film, resulting in scuffing and welding from metal contact.

Under the conditions (load of 294 N, speed of 1200 rpm, at room temperature for 30 min), the anti-wear property of triester derivatives and mineral oil 250BS were determined by the Wear Scar Diameter (WSD) as shown in Fig. 5. It was observed that, with the chain length increase of anhydrides, the WSD values first increased and then decreased, while the friction coefficient first decreased and then increased. AWCO has the smallest WSD, while i-BWCO has the lowest friction coefficient. One possible reason may be the increased film thickness because of the increase in molecular weight as a result of long branching groups.

**SEM analysis of worn surfaces:** Analysis of worn steel surface characteristics provides a wealth of information on the extent of wear protection by lubricants. The extent of this wear is however influenced by triester derivatives and 250BS that make a stable thin molecular film which prevents metal-metal contact. This preventive mechanism is, however, lost at high load when the protective lubricant film is squeezed out

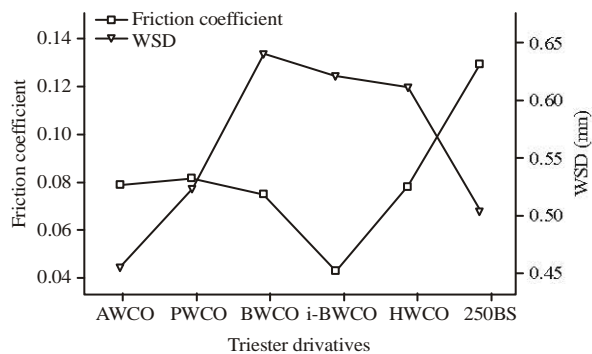


Fig. 5: Effect of the chain length increase of anhydrides on friction coefficient and WSD of steel ball. WSD: Wear scar diameter of the steel ball. The steel ball was lubricated by triester derivatives and 250BS under conditions: Load, 294 N; speed, 1200 rpm, room temperature; time, 30 min

between the metals, establishing contact (Erhan *et al.*, 2008; Salih *et al.*, 2011). Under the present experimental setup, the lubricant is allowed to flow between the metals and establish a stable film. The stability and tenacity of the film to adhere to the metal surface dictates the extent of its wear protection. Much of this stability is derived from the oil structure as observed from SEM analysis of wear track surfaces.

Figure 6 presents the SEM images of worn steel surfaces lubricated by triester derivatives and 250BS. It can be clearly observed that, under conditions (load, 294 N; speed, 1200 rpm; room temperature; time, 30 min), the worn steel surfaces lubricated by triester derivatives showed slight signs of wear and the worn scars were relatively shallow and smooth but when the worn steel surfaces were magnified 1000 times, it could be found out that the scuffed grooves on the surfaces were the most obvious upon being BWCO than other triester derivatives and 250BS. The wear profile with PWCO and 250BS are similar showing grooving with metallic flakes

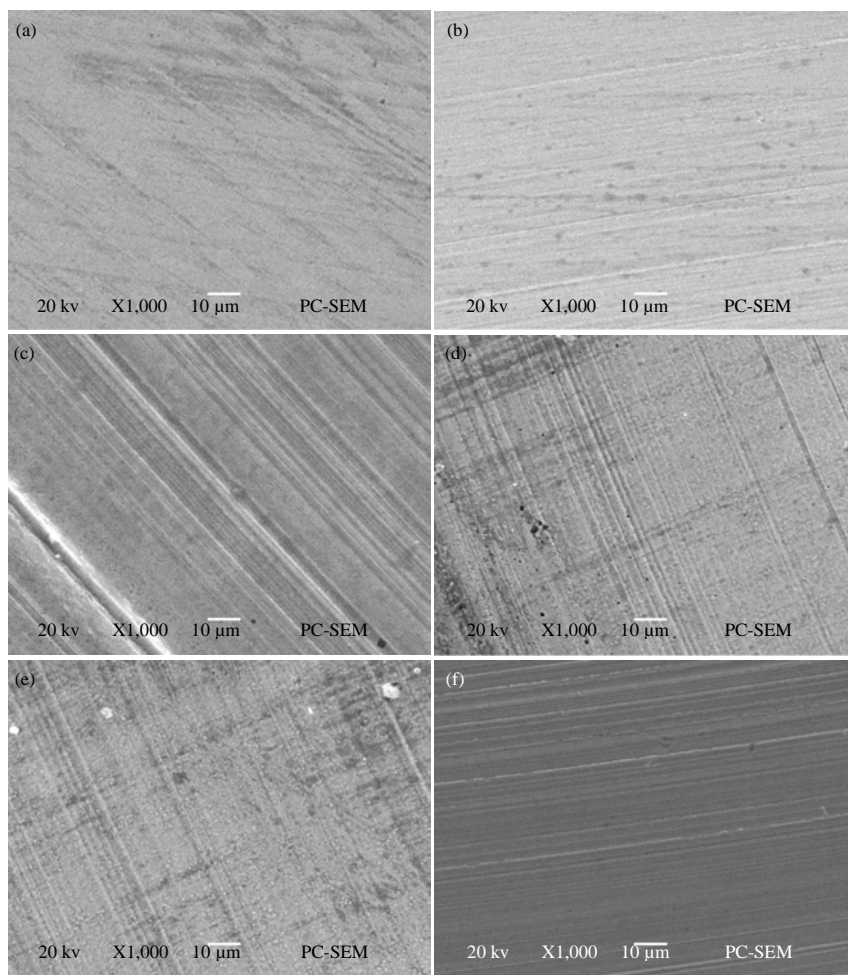


Fig. 6(a-f): SEM images of worn surfaces of steel ball. The steel ball was lubricated by triester derivatives and 250BS under conditions: Load, 294 N; speed, 1200 rpm; room temperature; time, 30 min. Triester derivatives: (a) AWCO, when  $R = -CH_3$ , (b) PWCO, when  $R = -C_2H_5$ , (c) BWCO, when  $R = -n-C_3H_7$ , (d) i-BWCO, when  $R = -CH-(CH_3)_2$ , (e) HWCO, when  $R = -C_5H_{11}$  and (f) 250BS, when  $R = -C_2H_5$

dislodged from the ball surfaces. This is also supported from Fig. 6, where both PWCO and 250BS show similar friction coefficients. With the chain length increase of anhydrides, the worn scars of steel balls became more and more deep and rough. Higher viscosity does not improve the lubricating properties significantly. Since there is no change in the polar functional groups in triester derivatives molecule, this does not translate into major improvement in boundary lubricating behavior.

### CONCLUSION

All triester derivatives from WCO shows better physicochemical properties, anti-wear ability and higher load-carrying capacity compared to 250BS, a representative of mineral oils. With the chain length increase of anhydrides, the viscosity and viscosity index of triester derivatives increased while the pour points decreased and no significant change was observed to the oxidation stability. With the chain length increase of anhydrides, the maximum nonseizure load ( $P_B$ ) of triester derivatives decreased, the friction coefficient and wear scar diameter decreased firstly and then increased and the worn scars of steel ball became more and more deep and rough.

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