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Lubricity Performance Evaluation of Organic Polymer as Additives Invegetable Oil Understeel Materials

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Abstract

The tribological effect of lubricating oil on sliding contact as well as its rheological behaviour were investigated. Using a high frequency reciprocating rig (HFRR) tribometer tester, the study applied Eichhornia Crassipes carboxymethyl cellulose (EC-CMC) polymer as an organic additive in corn oil (CO) and sunflower oil (SFO). Base CO and SFO samples were blended with four samples of EC-CMC concentration (0.5%, 1%, and 1.5%) by volume for the study of the viscosity improver index. Rheological studies on the polymer concentrations show good results with 1%, 2%, 3% and 4%, but indicated optimal on 1% EC-CMC especially from temperature beyond 100 ^{o}C for the two selected lubricants. Under friction and wear analysis, the test was conducted using 1wt% EC-CMC. The base lubricants CO and SFO yielded friction coefficient and wear scar diameter of 0.087, 11.2 *10^{-6} mm^3/N/m and 0.080, 10.5 * 10^{-6} mm^3/N/m, respectively. During the testing, the use of 1% EC-CMC blended SFO yielded lower coefficient of friction than CO both at base state and inclusion with additive. This produced COF reduction by 22.5% and 13.8% for EC-CMC + SFO and EC-CMC + CO, respectively, but gives better reduction under SAE 5W 30. The analysis concluded that application of 1% concentration of EC-CMC in base oil lubricant for both SFO and CO significantly enhanced the properties. The utilization of this sustainable product certainly will contribute to solving global pollution challenges.

Keywords: EC-CMC polymer, Vegetable oil, characterization, Friction, and wear.

1. Introduction

In recent years, researchers have been working to create environmentally friendly lubricants as a new alternative source due to worries regarding the use of petroleum-based lubricants and their effects on the environment. According to reports, spills, industrial waste, and marine engine exhaust gases result in the release of 5–10 million tons of petroleum products into the environment[1][2][3]. If nothing is done to protect the ecosystem from these problems, society will suffer, and a catastrophic calamity will result. In this regard, vegetable oil made from agricultural feedstock is viewed as a very attractive alternative to replace lubricating oil that is based on petroleum[1]. Vegetable oils have a lot of promise for usage as lubricants because they are biodegradable[4]. Although good number of bio-additives [5][6][7] for lubricants enhancement have been used in the past but they still require detail investigation to answer many questions, such as raw/synthesis material selection, tribological behavior on withstanding the working condition, especially on shear stability.

Analysis of the tribological behavior of carbon nanoparticles in vegetable lubricants for use in machining was carried out by Norfazillah et al.,[5]. The findings show tribological enhancement under application of activated carbon nanotubes when compared to base jatropha oil (JO) but recorded best performance when used modified jatropha oil with 0.025 % CNT (MJOa2) and considered suitable for metalworking fluid application. Investigation on the behavior towards friction improver as bio-lubricant additives was conducted [8]. Findings revealed that inclusion of polymeric viscosity improver (EVA copolymer) in palm kernel methyl ester (PKME)produced positive results towards the tribological properties, compared with base PKME oil. Most bio-lubricant products on the market today are made completely or partial from bio-based oils, provided these oils meet universal standards for biodegradability and non-toxicity.

Shalwan et al., [9] conducted tribological performance of different canola blended oil. The outcome showed that pure canola oil as a lubricant performed competitively against a blend of 80% synthetic and 20% canola oils. The analysis further stated that mixing ratio of canola and syntactic oil was

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not particularly significant since the pure canola oil exhibited competitive wear performance compared with the blends.

Corresponding to European requirements, a certified bio-lubricant needs to be at least 60% biodegradable and include at least 25% bio-based carbon[10]. The bio-lubricant must also be environmentally safe and appropriate for the application[4]. Several factors influence market demand for bio-lubricants, including consumer eco-friendly awareness, government regulations, and global lubricant demand[11]. Various functional vegetable lubricants have been developed with narrow views of the environmental impact issue due to the use of fossil-based additives in the formulation [12][13][14]. These lubricants can be made more sustainable by using all environmentally friendly and renewable base stock items. Many lubricants have been studied with various additives; the results produced both favorable and negative outcomes[15][16][17]. To improve the performance of the machine, it is important to know the appropriate base lubricant to use in combination with a given additive. Therefore, this present research uses corn and sunflower oil as vegetable oil together Eichhornia Crassipes bio-synthesized additive, as to ascertain their tribological behavior under different loading conditions. The commercial SAE-5W 30 oil was also used in the research as a reference.

2. Material and Methods

2.1. Base bio lubricant and Additive

Sunflower and corn oils purchased from Keck Seng (M) Sdn Bhd Malaysia were the vegetable oils used in this research. These oils have a semi-solid consistency at room temperature and a pour point of 23°C.The Eichhornia Crassipes carboxylmethyl polymer (EC-CMC) was synthesized in material laboratory of Universiti Teknologi Malaysia according to Opia et al., [18].The images of the base lubricants and additive used are presented in Figure 1.The information regarding the vegetable oil and EC-CMC polymer used in this research are described in Table I. They are considered inert, ecofriendly, and stable material. This experiment employed commercial SAE 5W 30 due to its good tribological performance.

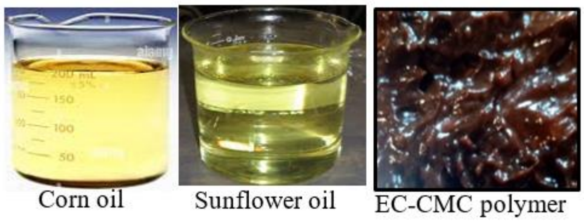

Figure 1. Images of base oil and additive used.

Table 1. Physical features of lubricants and additive used.

Properties	Corn oil	Sunflower oil	EC-CMC polymer
Appearance	Light yellow	Light yellow	Brown
State	Liquid	Liquid	Gelly semi-solid
Odor	odorless	odorless	odorless

2.2. Formulation of bio-lubricants used

The selected vegetable oil properties were presented by the producers. The various base oil was blended with different concentrations of EC-CMC polymer (0.5, 1 and 1.5 wt%). Based on recommendations from previous literature[18]and consideration of their environmental friendliness, the concentrations were chosen. Blends were made using 300 rpm of continuous speed mechanical stirrer with 200 ml each of corn and sunflower with polymeric additive. For about an hour, the blending procedure was conducted with a heating temperature of 80°C. The ratio of dynamic viscosity to lubricant density was blended to create the EC-CMC viscosity values. Subsequently, in accordance with ASTM D422, the viscosity indexes (VI) were obtained. *Thermo gravimetric analysis*(TGA) characterization was conducted on the formulations to ascertain the temperature resistance ability of the EC-CMC polymer.

2.3. Tribological Properties Analysis

In this study, a ball on flat tribo-tester device was used to investigate friction and anti-wear qualities for each formulation under ASTM-G133-05 standard test owing to its ability in producing accurate results as illustrated in Figure 2.It was anticipated that the load placed on the system would have this kind of an impact on the ball bearing's wear characteristics and friction behavior. In this set of tests, the tribological performance of EC-CMC copolymer was examined using raw vegetable oil. Standard ball bearings had a diameter of 10 mm, an HRC hardness of 64–66 RC, and were made of AISI E–52100 chrome alloy steel. Before each test, the surfaces of the balls and pot were cleaned with acetone to get rid of any traces of solvent that might still be present after the test lubricant is added. The wear specific rate of the flat steel used was calculated using equation 1. The operation conditions used in this study are presented in Table 2.

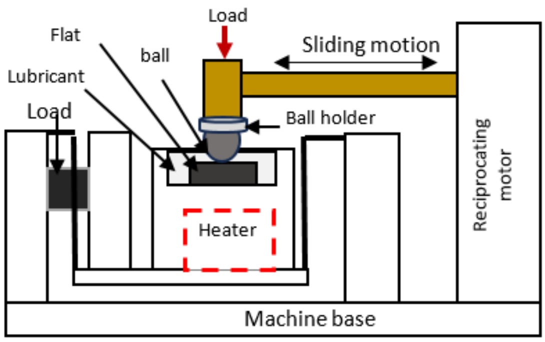

Figure 2. Schematic illustration of the HFRR machine with sliding mechanism.

Table 2. Testing working Conditions.

S/N	Detail	Description
1	Applied load (Kg)	40, 60, 80, 100and 120
2	Frequency	3 and 5 Hz
3	Duration	15 min
4	Temperature	55, 75, 100 and 120 ºC
5	Lubricant quantity	50 ml

$$Wear\ rate = \frac{Wear\ volume\ (m^3)}{Sliding\ distance\ (m)} \quad (1)$$

3. Results and Discussion

3.1. Morphological and Viscometric Evaluation of EC-CMC used.

For good physical understanding of the EC-CMC used, scanning electron microscope SEM analysis was performed. Figure 3displays a high resolution of EC-CMC. EC-CMC exhibited a gel-like form, as seen in the pictures. This result implies that the additives will be effective in application according to previous report [18].

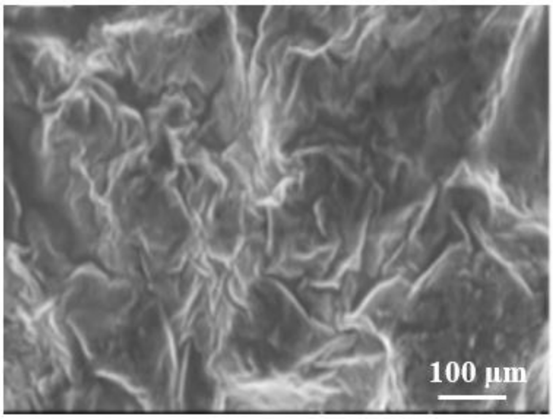

Figure 3. SEM morphological image of EC-CMC polymer used.

Figure 4 presents the kinematic viscosity results for each lubricant sample. In general, each sample's kinematic viscosity decreased as the temperature increases. This happened because of the intermolecular forces gradually weakening as temperature increased. The viscosity of the vegetable oil and the tested temperature have since been increased by the addition of polymeric viscosity modifiers (EC-CMC polymer). Through the application of heat, the concentration of various EC-CMC copolymers is controlled to bring back the kinematic viscosity of base corn and sunflower oil. Similarly, [19]presented the same reports in the investigatory research to resolve the poor viscosity issues onSFO and soybean oil.

The high VI values of corn and sunflower oils are really a result of the EC-CMC structure's ability to support the oils' potent intermolecular interactions as temperature increases. However, because of severe thermal effect on the lubricant, the added polymereventually loses its polymeric straight [20]. According to the research, the viscosity index (VI) value rises as polymers are incorporated into the lubricating oil, yet 1 wt.% EC-CMC exhibits the lowest VI of all the polymer concentrations tested. Though lubricants during operation, viscosity reduces as temperature rises, polymer molecules stretch[20], thus, the micelle becomes larger as a result. The viscosity of the polymer-doped lubricants oil is balanced by the larger micelles created by concentrations.

Figure 5 shows the TGA results of base sunflower oil, base corn oil, SF + EC-CMC and CO + EC-CMC. The weight loss proportion was revealed using derivative thermos-gravimetric information[21]. The thermos-gravimetric curve's intersection of two tangents provided the onset degradation temperature, which was found right before the inclination brought on by degradation from different EC-samples. Base sunflower oil weight loss was 38.5%, while base corn oil weight loss was 36.3%, which could be assigned to impurities adsorbed during preparation. After being modified, the SF + EC-CMC weight loss was 18%, according to Figure 3. The changes suggest that the thermal properties of sunflower and corn oil have been improved due to thermal degradation resistance from EC-CMC. The modified CO + EC-CMC resulted in a 14.7% weight loss. Compared to base SFO and CO, the weight loss of SF + EC-CMC and CO + EC-CMC were significantly lower, which may be attributed to the synthesis procedure, leading to improved thermal properties.

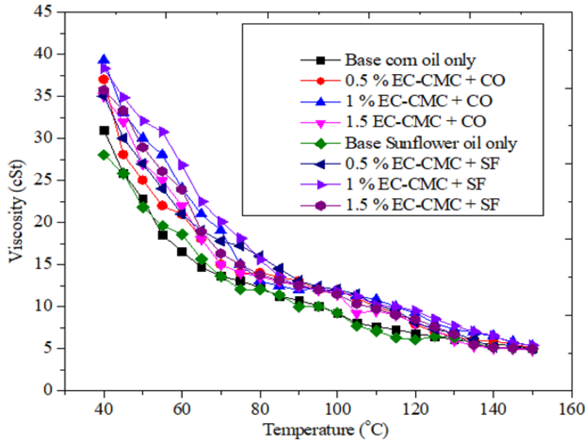

Figure 4. Viscosity-Temperature analysis of the base oil without and with additive.

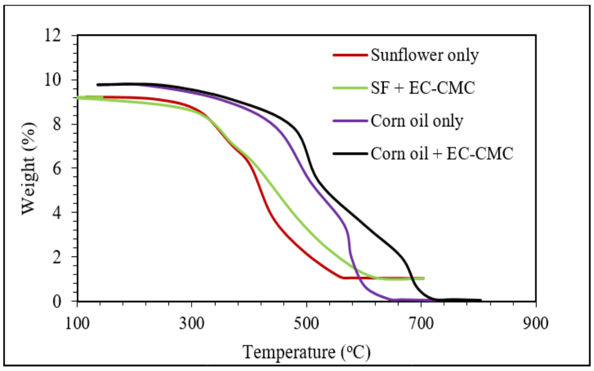

Figure 5. TGA results of sunflower and corn oil without an addition of EC-CMC, indicating the weight loss over temperature.

Table 3. Lubricant samples tribological properties values

Lubricant	Specific gravity @ 25 °C	Viscosity (cSt)			Viscosity Index (VI)
		@ 40 °C	@ 100 °C	@ 150 °C	
Corn oil	0.889	31.02	9.3	5.01	306.33
0.5% EC-CMC + CO	0.978	37	12	5.1	337.36
1% EC-CMC + CO	0.992	39.3	11.7	5.3	309.30
1.5% EC-CMC + CO	1.0461	39.9	11.5	4.8	314.03
Sunflower oil	0.090	30.02	9.01	5.01	307.72
0.5% EC-CMC + SF	0.994	35	12.01	5.13	357.59
1% EC-CMC + SF	0.999	38.3	11.77	5.43	318.84
1.5% EC-CMC + SF	1.038	35.7	11.45	4.98	323.38

3.2. Frictional analysis

Figure 6(a and b) shows the friction coefficients and wear rate of the various lubricants under load of 80 N and temperature of 75°C at frequency of 5Hz. The base sunflower oil lubricant average COF was 0.080, while base corn oil was 0.087 as illustrated in Figure6 (a). When added polymer, SFO + 1% EC-CMC and CO + 15 EC-CMC yielded average COF of 0.0.062 and 0.075, respectively compared to SEA -5W 30 of 0.056. The COF were reduced by 22.5% and 13.8% against base sunflower oil (0.080) and corn oil (0.087), respectively. Base sunflower and corn oils have a greater coefficient of friction during the test because the hydrodynamic pressure of the oil layer is constrained. Comparing EC-CMC to commercial SAE-5W-30 lubricant, the friction coefficients were noticeably greater for the former. The behavior of EC-CMC with the two selected base vegetable oil at frequency of 3 Hz, gives similar outcome with previous literature[22]. Obviously, the outcome could be of good compatibility between the additive molecules, possibly having average molecular weight, resulting in good tribo-film formation and a lower COF.

The wear rate on the ball used on the various lubricants were presented in Figure 6 (b). The inclusion of the 1 wt.% polymer demonstrated wear reduction on the ball samples. The wear rate of base sunflower and corn oil only were 10.5 and 11.2 (10^{-6} mm^3/N/m), respectively, while SFO + 1% EC-CMC yielded 6.8 10^{-6} mm^3 /N/m) and CO + 1% EC-CMC gives 7.1 10^{-6} mm^3 /N/m), indicating good wear rate reduction. However, the commercial SEA 5W-30 lubricant exhibited superior performance with 6.5 10^{-6} mm^3 /N/m).

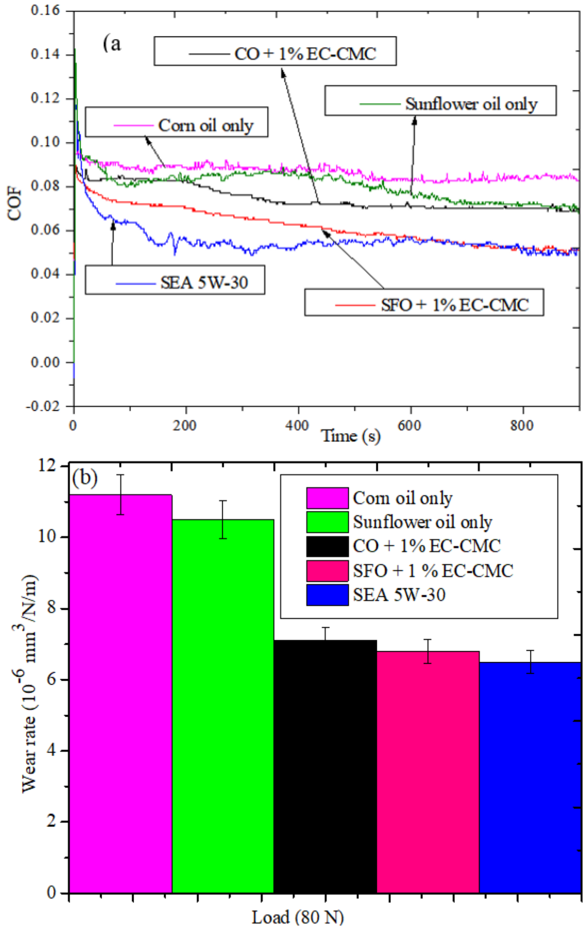

Figure 6. Analysis COF (a) and wear rate (b) of sliding the various lubricants under 80 N, frequency of 5Hzunder 15 min. operation.

The mean COF and wear rates of base sunflower and corn oil also the SFO + 1% EC-CMM and CO + 1% EC-CMC calculated under sliding frequency of 5Hz are shown in Figure 7(a and b). At 5 Hz under 40, 60, 80, 100 and 120N with inclusion of EC-CMC show enhanced COF better than the base lubricants used as shown in Figure7(a). However, application of SEA 5W 30 exhibited the best result in COF reduction, followed by SFO + 1% EC-CMC. The average COF for sunflower and corn oil under 40, 60, 80, 100 and 120 N were 0.075, 0.073, 0.080, 0.088,0.091 and 0.085, 0.084, 0.087, 0.093, 0.096, respectively. When referring to the behavior, the COF behaviors follow a similar pattern.

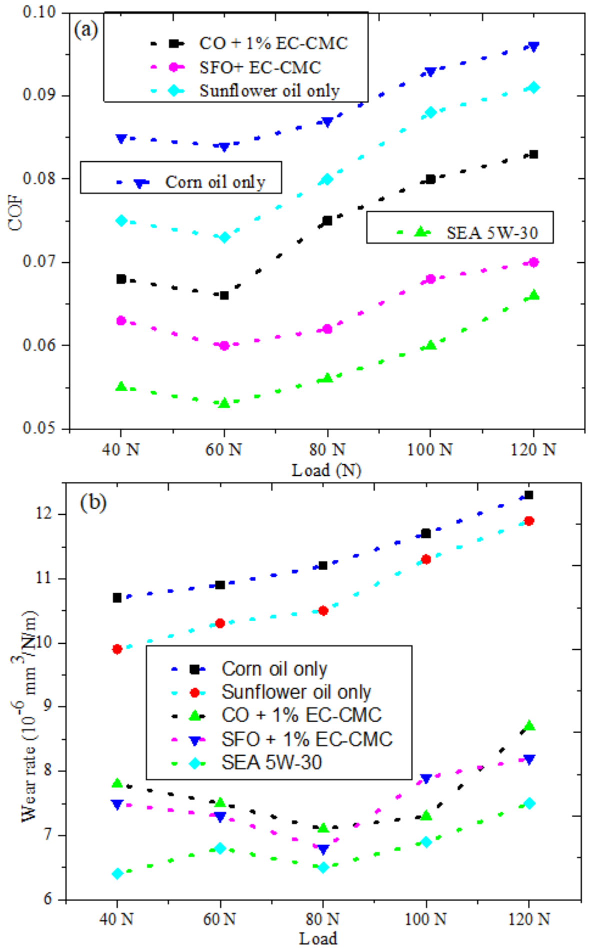

Figure 7. Average coefficient of friction (a), and wear rates (b) of base corn and sunflower oil and inclusion of EC-CMC under different loads (40, 60, 80 and 100 N) at temperature of 75 °C.

As revealed in Figure7(b), the wear rate of the various tested samples of base lubricants increases with increase in the applied load, however, with addition of polymer, all the values reduced at 80 N but increases with 100 and 120 N. The study concluded that 80 N gives the best performance with the polymer in the selected base lubricant, thus considered best load for the EC-CMC polymer. The conversion of the sliding action into rolling could be the cause of the improved performance from EC-CMC. The findings are consistent with earlier research [22][23], in that adding reinforcing fibers significantly improves the wear resistance of polyimide (PI) when it is lubricated with oil.

3.3. Tribo-pair worn surfaces analysis

Figure 8 shows the results of utilizing a low-resolution microscope SEM to examine the worn scar images of the flat specimen. The analysis focuses on the flat surfacetoascertain the working characteristics of each lubricant. As statedpreviously, base samples of CO and SF exhibit the worst performance demonstrating large grooves on the sliding surfaces. Meanwhile, 1% EC-CMC blended CO and SF produce comparable performance with the SAE-W5-30 commercial product.As shown in the Figure 5, furrows can be observed all the tested lubricant, indicating that abrasive plowing was a wear manner on the steel plate lubricated. The wear was much on base lubricant followed the inclusion of EC-CMC additives before the commercial SAE-W5-30 lubricant. Each friction surface had a different abrasive ploughing, respectively. The friction surface under corn oil had the deepest furrows, indicating poor film formation.The wear behavior observed were similar with previous literature analysis [24].

For the depth of the wear track and the cross-section profiles of the different lubricants are shown in Figure 9. As demonstrated by the lubricants, base samples show the highest surface roughness and wear depth before the samples with EC-CMC additives. The minimum wear depth was obtained with the commercial SAE 5W 30 lubricants. Investigating the depth reduction under EC-CMC polymer when applied on various vegetable oils. The result showed that EC-CMC + corn oil exhibits better wear depth reduction than EC-CMC + sunflower oil. This is similar to the observation recorded in the previous work [15].The analysis showed 98 µm and 102 µm wear depth for EC-CMC + corn oil and EC-CMC + sunflower oil, against depth value of 321 nm and 332 nm of base corn oil and sunflower oil, respectively. These results show a close relationship between WSD and wear depth behaviors, of EC-CMC + corn oil and EC-CMC + sunflower as demonstrated in Figure 9.

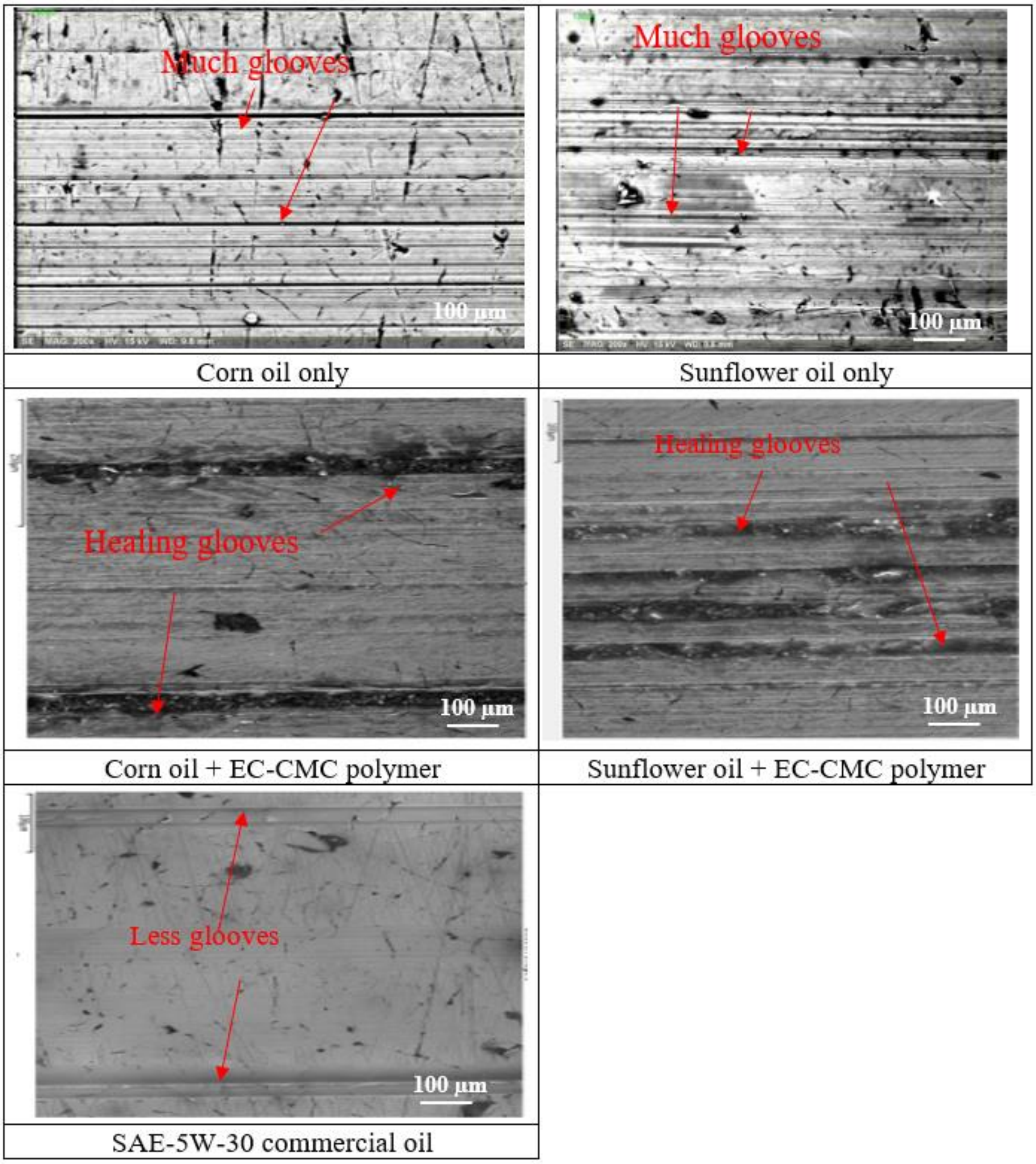

Figure 8. Wear scar surfaces of the steel plat lubricated with different lubricants; a) Corn oil only; b) Sunflower oil only; c) Corn oil + EC-CMC polymer; d) Sunflower oil + EC-CMC polymer; e) SAE-5W-30 commercial oil.

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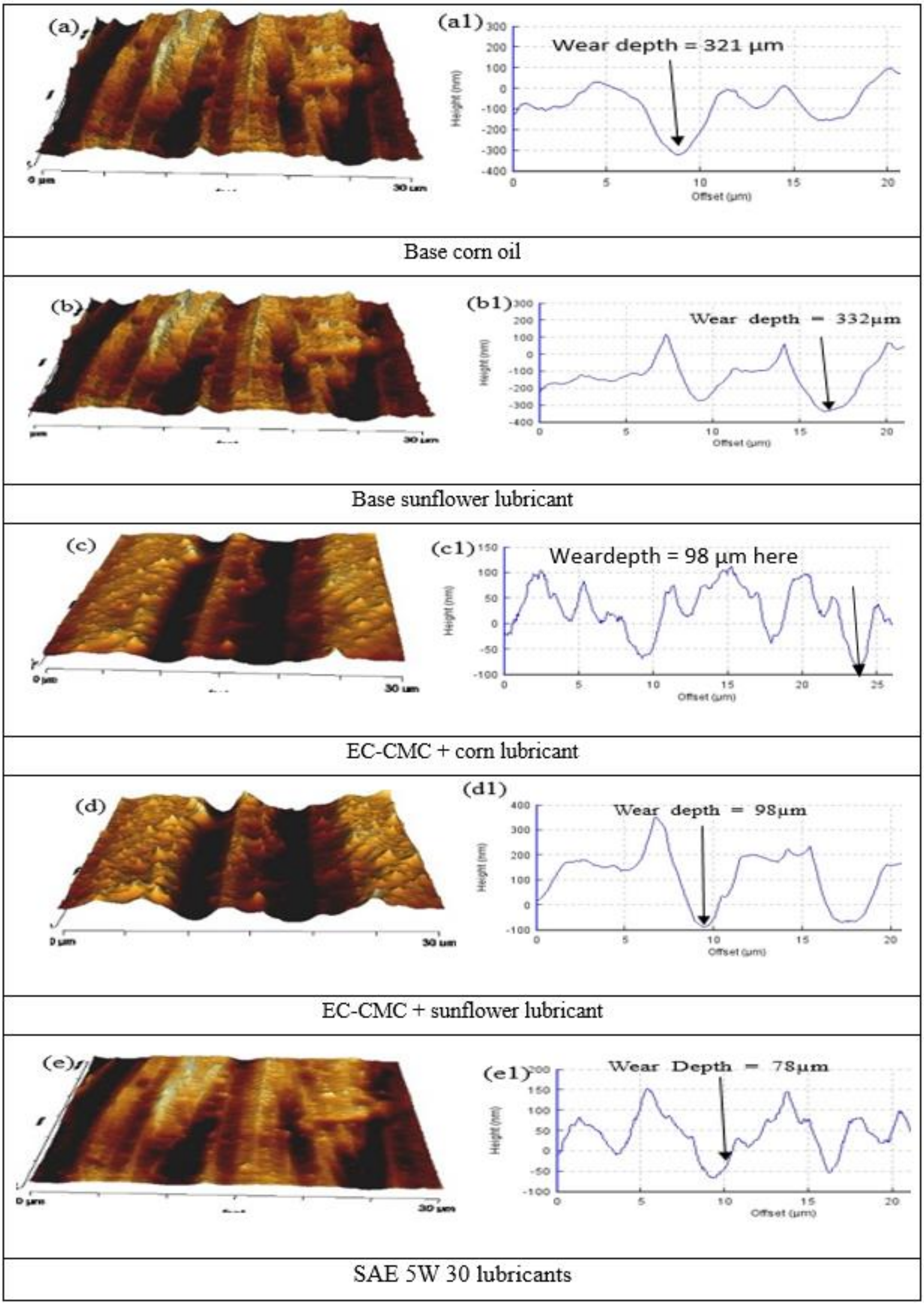

Figure 9. 3D images (a-e) and cross-section profiles (a1-e1) of the lubricated surface with the various lubricant (base SF (a-a1); base CO (b-b1); 1 wt.% EC-CMC + SF (c-c1); 1 wt.% EC-CMC (d-d1); and SAE W5 30 (e-e1).

4. Conclusion

The requirement for bio-based additives to replace inorganic based additives in lubricant compositions for any sliding contact (quantity depletion and environmental impact). This is in accordance with international sustainability initiatives that emphasize the use of socially problematic materials to address human needs. To improve the tribological properties of corn and sunflower oil, the EC-CMC polymer was suggested, described, and used. To compare the two different oils, tribological enhancement was carefully examined in terms of coefficient of friction and wear scar rate. The final characteristics were compared to SAE-W5-30, a commercial standard. The findings showed that under 5Hz operation, the COF were reduced by 22.5%, and 13.8% for sunflower and corn oil respectively, while wear scar rate for sunflower and corn oil blended with 1 wt.% EC-CMC were 6.8 and 7.1 (10^{-6} mm^3 mm/N/m), respectively compared base value of 10.5 and 11.2 (10^{-6} mm^3 mm/N/m), while SEAW5-30 yielded 6.5 $*10^{-6}$ mm^3 mm/N/m, thus observed comparable. The experiment finally deduced that EC-CMC operation with sunflower was more effective than corn oil, thus suggesting it can be applied in place of SEA-W5-30 lubricant.

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