Comparative Evaluation of Biodegradable additives of Ethyl Cellulose (EC) and Ethylene Vinyl Acetate (EVA) on Tribological Properties of MBS Oil.

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Abstract
The effect of biodegradable additives of Ethyl cellulose (EC) and Ethylene Vinyl Acetate (EVA) on tribological properties of oil extracted from banana peel waste of Musa *Aluminata Balbisiana* (MBS) was evaluated. The presence of EC and EVA at difference strength of concentration leads to reduction in COF, WSD and *Ws* values for MBS oil. The addition of 4.0% w/w of EC and EVA in pure MBS oil at the parameter of 27 ºC and 100 N of applied load were lead to reduction in WSD and *Ws*. However, unlike with the COF results, addition of EC and EVA on MBS oil did not show very significant reduction either in WSD or in *Ws*. Therefore, they would not effectively act as anti-wear properties. It can be inferred that, at the low temperatures and strength, EC is more effectives to lead to the reduction of COF in MBS oil than EVA. Lower COF values of MBS oil with presence of additive of EC and EVA suggest that the indicative of the formation of protective tribo-chemical film, which was promoted by the tribochemical reaction due to the rubbing action and chemical interaction of EC and EVA with MBS oil. MBS oil with addition of EC showed a very stable COF value compared to the addition of EVA is reflected to the strength of the boundary film formed by the oil on the surface. Surface morphology analysis on the spherical pin used in pin on disc in tribological procedures were shown to have a predominant wear mechanisms of adhesive and abrasive wear.

Keyword: Biodegradable additives, Ethyl Cellulose, Ethylene Vinyl Acetate, Tribological Properties, Coefficient of Friction, Wear Scar Diameter, Wear Mechanism.

1.0 Introduction

Vegetables oil had offered a promising property of renewable, biodegradable, economically cost effectives and has no adverse effects on the environment (Ing et al., 2012; Asadauskas and Erhan, 1999). Studied had showed that oil extracted from many oil crops, such as soybean, sunflower, castor bean and others are possessing structurally similar to petroleum-based oils, which composed of long chain hydrocarbons and it possess many excellent properties, which are suitable for lubricant applications (Salimon and Salih, 2009). The existence of high polarity compounds such as chemical composition of polyester and unsaturated fatty acids in vegetables oils were believed to contribute to the good lubricating properties (Petlyuk and Adams, 2004). The good lubricating properties of vegetables oils was believed to provide a high strength of lubrication film and it will provide a strong force and interactions between the metallic surface (Quinchia et al., 2014; Fox and Stachowiak, 2007). Unfortunately, despite having the good lubricating properties, vegetables based lubricants display its own withdrawal characteristics. Easily undergo an oxidation process is one of the major weakness of vegetables oil. This is due to the existing of double bond to the oxygen linkage in their chemical structures. This condition however could lead to the failures in tribological properties which would affects the frictions and wear behaviors (Md Alias and Azhari,2017; Mannan et al., 2017). Therefore, to overcome these poor tribological characteristics in vegetable oils, additives compounds have been introduced.

Biodegradable additives are defined as a natural or synthetic chemical substances mixed which was added with base oils, which functioned to improve various characteristics of lubricants so the oils can placate the higher demand placed on them and satisfy specification requirements. In current study, biodegradable and environmental friendly of additives Ethyl Cellulose (EC) and Ethylene Vinyl Acetate (EVA) were chosen. In nature, EC and EVA both possess and considered as an inert, nontoxic and stable materials (Quinchia et al., 2014). The introduction of EC and EVA was believed to improve some of the shortcomings and withdrawal effect of vegetables oil Quinchia et al., 2009; Quinchia et al., 2010; Quinchia et al., 2011 and Quinchia et al., 2012). Quinchia *et al.*, 2010 *had* been scientifically reviewed the potential effect of EC and EVA copolymer. The results were shown that, addition of 1% (w/w) of EC into the vegetables oils had resulted in important increasing in oil viscosity within the temperatures ranged studies. However, addition of EVA was successfully tested as viscosity modifier for several vegetable oils and was yielding potentially environmental friendly lubricants for some applications.

This paper is focus on the comparative evaluation of biodegradable additives on tribological properties of MBS oil extracted from banana peel waste of Musa *Aluminata Balbisiana* using Ethyl cellulose (EC) and Ethylene Vinyl Acetate (EVA). The optimum parameter for the tribological testing was optimize using Taguchi Method and further confirmed through experimentally. The tribological results of coefficient of friction (COF), wear scar diameter (WSD) and Wear rate (*Ws*) were evaluated as a comparative comparison between EC and EVA on tribological properties of MBS oil.

2.0 Methodology

2.1 Optimization Control Factors using Taguchi Method

In this study, optimization parameter for was determined using Taguchi Method. Percentages of biodegradable additives, temperatures and applied load with three levels were considered as a control factors and was detailed in Table 1. A Minitab 17 software was used for the selection of the orthogonal array. A L9 orthogonal array was selected and details of the experiments was shown in Table 2. Three columns were considered and each consists of three levels. The plan of experiments includes 9 row experiments was assigned to the control factors. Responses taken during the experiment were friction coefficient, COF, and wear rate, *Ws* (mm^2 /N).

Table 1: Factors and levels considered during the plan of the study

Factors	Level I	Level II	Level III
% of Biodegradable Additives (EC/EVA)(C)	0.5	2.5	4
Temp.,°C, (T)	27	40	100
Applied Load, N, (F)	60	80	100

Table 2: L9 orthogonal array of Taguchi Method

Exp. No.	% of Biodegradable Additives (EC/EVA)(C)	Temp.,°C (T)	Applied Load,N(F)
1	0.5	27	60
2	0.5	40	80
3	0.5	100	100
4	2.5	27	80
5	2.5	40	100
6	2.5	100	60
7	4.0	27	100
8	4.0	40	60
9	4.0	100	80

2.2 Sample Preparation.

In this study, MBS oil with addition of EC and EVA at the concentration of 0.5%, 2.5% and 4.0% (w/v) were prepared and shown in schematic diagram below (Figure 1). An approximately about 15.0 g, 75.0 g and 120 g of biodegradable additive of EC and EVA were respectively added into of MBS oil. The mixtures then were stirred continuously at the constant speed of 150 rpm. The slurry mixtures then were heat up at the temperature of 120 -150 °C for 1 hours. The homogenous samples mixtures were let to cool down to room temperature. Before proceed to tribological analysis, the samples were prepared according characteristic of L9 orthogonal array of Taguchi Method as tabulated in the Table 2.

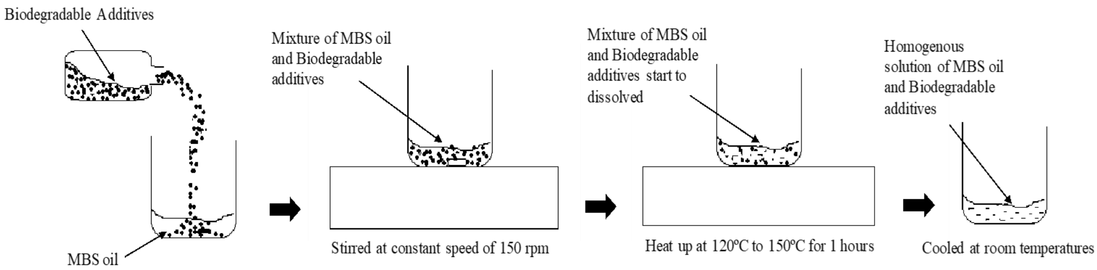

Figure 1: Schematic diagram of preparation of MBS oil with biodegradable additives

2.3 Tribological Procedures

The experimental procedures of tribological properties was performed using pin-on-disc tribometer according to the ASTM G99-05 Standard under wet sliding conditions and it was illustrated in schematic diagram in Figure 2 below. The test parameter for this study was set according to the L9 orthogonal array of Taguchi Method in Table 2. Sliding speed of 50 RPM, sliding constant at 314m and sliding time for 50 minutes were set at constant values for the entire process. A hemisphere pin was held firmly against a rotating disc which had been connected to a certain dead weight with a beam and two pulleys. The 2 mL of samples were placed on the disc surface respectively. The windocom 2008 software was used to record the data from the pin on disc machine. The pin was heated using an external heat resource where a thermocouple was placed on the edge of the counterpart pin. Time was set according to the time of test that would be conducted. An infrared thermometer (Extech 42580) was used to measure the temperature. During the experiment, a hemispherical pin was clamped against the rotating disc. Each of the testing was repeated for three times to minimize experimental errors.

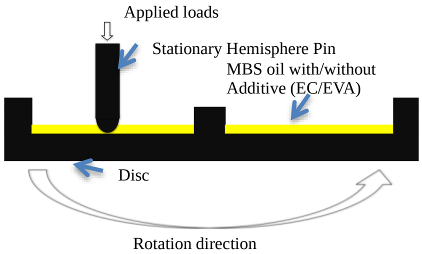

Figure 2: Schematic diagram of pin on disc.

2.3 Calculation of Coefficient of Friction (COF) and Specific Wear Rate (*Ws*)

The value of COF and *Ws* were calculated based on Eq. (1), Eq. (2) and Eq. (3) below:

$$F = \frac{F}{W} \tag{1}$$

$$Ws = \frac{\text{Vloss}}{\text{WxL}} \tag{2}$$

$$Vloss = \frac{\pi d^4}{64R} \tag{3}$$

Where, F = frictional force; W= applied load (both F and W units are in N); *Ws* = specific wear rate (mm^3/Nm); L = sliding distance (m); *Vloss*= wear volume losses of the pins; d= wear scar diameter in unit of meter; R= radius of the pin (fixed value at 0.00149 m).

2.4 Surface Morphology

Wear morphology and characterization analysis of the pin surface were carried out using SEM. Images analyses were obtained using Carl Zeiss Scanning Electron Microscope- EVO/MA 10 model coupled with Energy Dispersive X-ray Spectrometer (EDS). In this method, the electron in the beam was interacted with the samples producing various signals that can be used to obtain information about the surface topography and information. Samples already screened to a size of 125 μm were attached to multi-stub sample holder with the use of double-sided conductive carbon tape after which it was mounted onto the specimen chamber. The specimen chamber and column were kept under vacuum. After reaching the vacuum target, the electron gun was switched on and accelerating the voltage of 20 kV, probe current of 227 pA and working distance of 8.5 mm were maintained during the entire procedures.

3.0 Results and Discussion

3.1 COF Analysis

The presence of biodegradable additive of EC and EVA play a role in reduction of COF. Figure 3 shows a variation of COF values with the presence of EC and EVA at difference concentration (% w/w). Addition of 0.5% w/w of EC and EVA on MBS oil shows a variation in its COF values as compared to MBS oil without addition of additives. At Experiment 1 (27 ºC and 60 N), the presence of 0.5% w/w of EC and EVA lead to the 33.7% and 73.3% decrement of COF values respectively as compared to MBS oil. Meanwhile, for Experiment 2 (27 ºC and 60 N), 0.5% of EC and EVA lead to reduction of COF at the 60.7% and 35.6% respectively. However, at the 100ºC and100 N (Experiment 3), the presence of EC and EVA at the strength of 0.5% w/w did not affect the COF values of MBS oil. This result indicated that, the presence of 0.5% (w/w) of EC in MBS oil results in very different lubrication regimes distribution, which exhibited significantly reduction in COF values. By contrast, the presence of EC would suggest to effect on the boundary friction (Quinchia *et al*., 2014). On the other hand, the addition of 0.5% (w/w) of EVA had a little effect compared to EC. This seem to demonstrate that there is no boundary film was formed with 0.5% (w/w) EVA.

Meanwhile, addition of 2.5% w/w of EC to the MBS oil lead to the reduction of COF values with 4.1% (Experiment 5, 40 ºC, 100 N). For Experiment 6 (100 ºC, 60 N), presence of EC was lead to the 16.8% of decrement in COF values. Meanwhile, addition of 2.5% w/w of EC at 40 ºC, 100 N (Experiment 5) and 100 ºC, 60 N (experiment 6) were lead to the decrement in COF values with the reduction values of 4.1% and 16.8% respectively. However, at 27 ºC, 80 N (Experiment 4), there are no significant effect was observed. For EVA, it was noted that, there are no significant reduction in COF values for all the tested parameter in Experiment 4, experiment 5 and Experiment 6.

For 4.0% of w/w of EC and EVA was noticed to show a decrement in COF values. At 27 ºC and 100 N (Experiment 7), decrement of COF values was noticed at the values of 19.4% and 29.1% respectively. For 40ºC and 60 N (Experiment 8), only addition of EVA on MBS oil showed a decrement values in COF at 15.01%. Meanwhile, at 100ºC and 80 N (Experiment 9), both EC and EVA showed a decrement in COF value with the reduction value of 8.4% and 41.5% respectively.

The presence of EC and EVA at difference strength of concentration leads to reduction in COF values for MBS oil. Besides, it can be inferred that, at the low temperatures and strength, EC is more effectives to lead to the reduction of COF in MBS oil than EVA. Lower COF values of MBS oil with presence of additive of EC and EVA suggest that the indicative of the formation of protective tribo-chemical film, which was promoted by the tribochemical reaction due to the rubbing action (Quinchia *et al*., 2014) and chemical interaction of EC and EVA with MBS oil. MBS oil with addition of EC showed a very stable COF value compared to the addition of EVA is reflected to the strength of the boundary film formed by the oil on the surface. Tribo-chemical interaction of fatty acid compositions particularly with a high percentage of SFAs and

MUFAs in MBS oil affect the strength of the boundary film thus lead to strong protective film formed and stable over time and therefore more effective (Asadauskas *et al*., 1996).

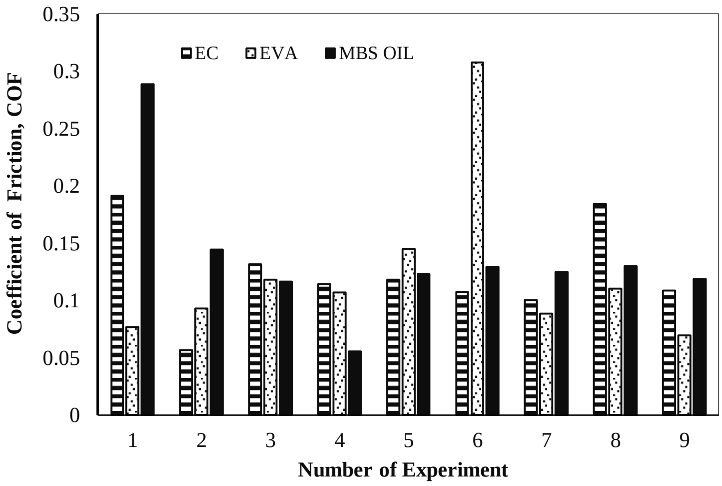

Figure 3: Variation of COF Value of MBS Oil with the Presence of EC and EVA at Different Concentration

3.2 Wear Scar Diameter, WSD and Wear Rate, *Ws* Analysis

In wear analysis, applied load has been shown to affect oil film formation between mating contact, which will affect the development of friction, and wear (Manabe and Nakano, 2008). In this study, the effect of 0.5, 2.5 and 4.0 % w/w of EC and EVA at the temperature range of 27 ºC - 100 ºC and 60 N - 100 N of applied load of MBS oil on wear scar diameter analysis and wear rate, *Ws* analysis were investigated. The variation of WSD and *Ws* results were depicted in Figure 4, Figure 5 and Figure 6 below. Based on results shown, EC and EVA at all the tested parameter did not shown any good effect in reduction of WSD and *Ws* except for Experiment 7 (4.0% w/w, 27ºC, 100 N) for EC and Experiment 1 (0.5% w/w, 27 ºC, 60 N), Experiment 3 (0.5% w/w, 100 ºC, 100 N) and Experiment 7 (4.0% w/w, 27 ºC, 100 N) for EVA.

All the optimized concentration of EC at tested parameter were shown almost no effect in reduction of WSD and *Ws* in MBS oil expect for 4.0% at temperatures of 27 ºC and load of 100 N. Addition of 4.0% of EC at the temperatures of 27 ºC and load of 100 N lead to decrement in WSD and *Ws* at the values of 40.7 % and 8.78% respectively as compared to pure MBS oil. Based on the results shown, Experiment 7 was shown to have a higher decrement in WSD and *Ws* values for addition of EC in pure MBS oil. At this tested parameter, the tribochemical reaction may occur between the chemical composition of EC and fatty acids composition, which contained in pure MBS oil. The synergetic effect between these composition lead to the formation of protective film on the surface thus prevent the surface from contacted to each other's and resulted in lower values of WSD and *Ws*. The wear mechanism of mentioned EC concentration at the tested parameter was discussed in detail in wear mechanism 4.5.3.3.

Moreover, a concentration on 0.5% w/w of EVA at temperatures of 27 ºC and load of 60 N (Experiment 1) and 100 N (Experiment 3) would lead to decrement in WSD and *Ws*. At the tested parameter in Experiment 1, the strength of 0.5% w/w EVA would decrease the WSD and *Ws* with decrement value of 20.1 % and 6.01 % respectively. Meanwhile, at 27 ºC and load of and 100 N (Experiment 3), WSD and *Ws* were noticed to inhibit the decrement with the percentage decrement of 22.1% and 1.47% respectively. In addition, 4.0% w/w of EVA at 27 ºC and 100 N (Experiment 7) of load also had shown a capability to decrease the WSD and *Ws* with the % decrement value of 44.9 % and 9.16% respectively. Based on the result shown, Experiment 7 displayed a highest decrement in WSD and Ws for addition of EVA in MBS oil. The wear mechanism of Experiment 1, 3 and 7 were briefly discussed in wear mechanism 4.5.3.3.

In summary, the addition of 4.0% w/w of EC and EVA in pure MBS oil at the temperatures of 27 ºC and load of 100 N were lead to reduction in WSD and *Ws*. However, unlike with the COF results, addition of EC and EVA on MBS oil did not show very significant reduction either in WSD or in *Ws*. Therefore, they would not effectively act as anti-wear properties.

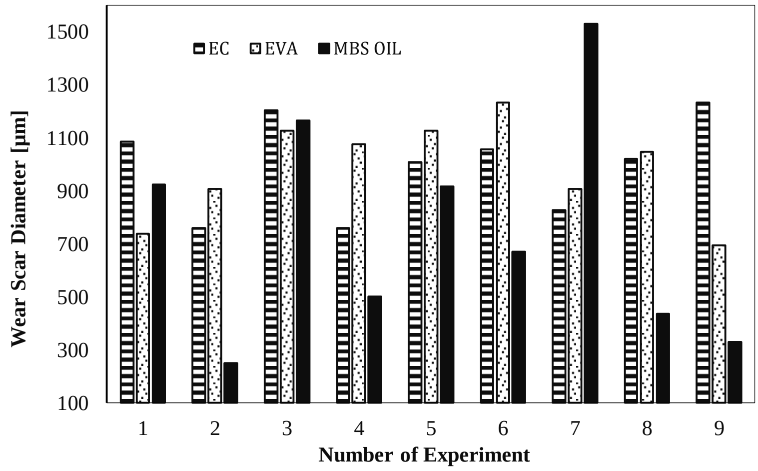

Figure 4: Variation Value of Wear Scar Diameter of MBS Oil with the presence of EC and EVA at Different Concentration.

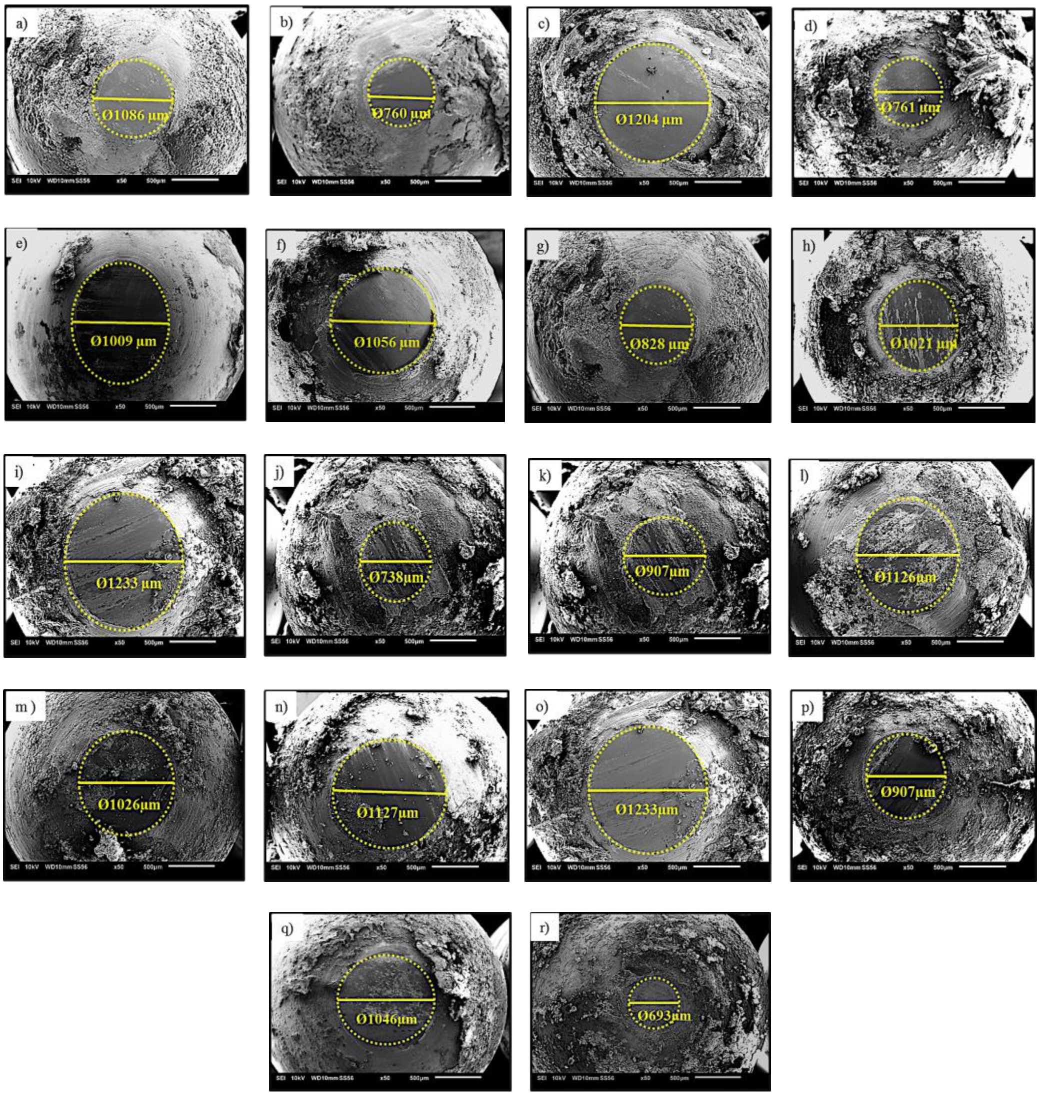

Figure 5: SEM Micrograph of Worn Surface of Hemisphere Pin at the Presence of EC (a-i) and EVA (j-r) at Different Concentration.

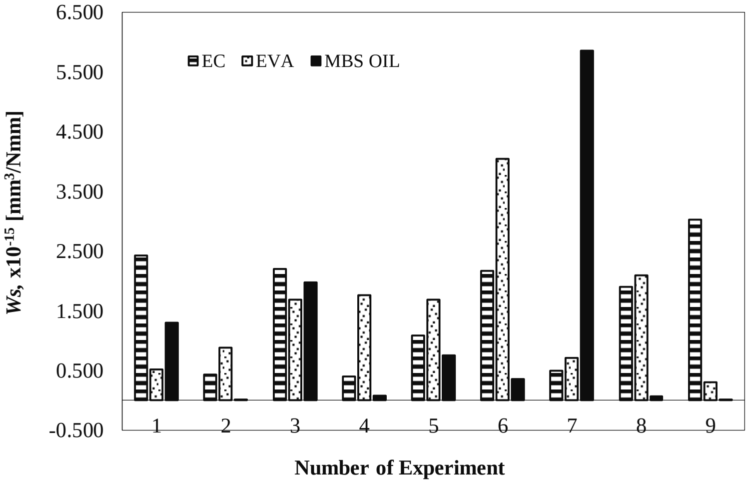

Figure 6: Variation Value of Wear Rate, *Ws* of MBS Oil with the Presence of EC and EVA at Different Concentration.

3.3 Wear Mechanisms

Figure 4.32a and Figure 4.32b presents wear mechanism for addition of 4.0% w/w of EC at 27 ºC and load of 100 N (Experiment 7). Figure 4.33a and Figure 4.33b were showed a wear mechanism of EVA at 0.5% w/w at 27 ºC and load of 60 N (Experiment 1), while Figure 4.34a and Figure 4.34b were depicted a 0.5% w/w of EVA at the 27 ºC and load of 100 N (Experiment 3) and Figure 4.35a and Figure 4.35b were depicted the wear mechanism of EVA at 4.0% w/w at 27 ºC, load of 100 N (Experiment 7) which were observed using SEM. The images of worn surface were analysed using SEM-EDX spectroscopic. Figure 4.32a show the worn surface micrograph of for addition of 4.0% w/w of EC at 27 ºC and load of 100 N (Experiment 7). The micrograph indicates that, the worn surface lubricated with addition of 4.0% w/w of EC was characterized by abrasive wear, which form scratch and formed a groove on the pin surface. These effects occur due to displacement away of materials from the wear particles and it was clearly shown by the EDX images in Figure 4.32b. Figure 4.33a and Figure 4.35b were presented the worn surface of 0.5% (Experiment 1) and 4.0% w/w (Experimnet 7) of EVA at the fixed temperature of 27 ºC and load of 60 N and 100 N respectively. At both parameter, the worn morphology analysis by SEM micrograph shown that, the surface was dominated by abrasive wear and their dislocation of materials from the wear particles were shown in Figure 4.33b and Figure 4.35b respectively. Furthermore, Figure 3.34a shown the worn surface of 0.5% w/w of EVA at the temperatures of 27 ºC and load of 100 N (Experiment 3). At this parameter, the worn surface was characterized by adhesive wear. The adhesive wear phenomenon occurs due to the plastic deformation whereby at this region, wear debris and materials particularly chemical composition present in MBS oil were attached together on the worn contact surface due to the high contact pressures caused by the 100 N of load. The wear debris from adhesive wear was illustrated in Figure 4.34b.

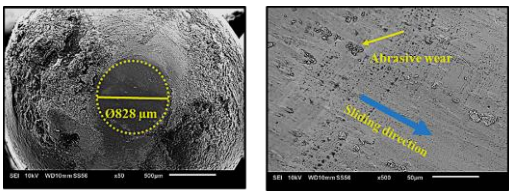

Figure 4.32a**:** Worm Surface and Wear Mechanism on the Hemispherical Pin with Addition of 4.0% w/w of EC at 27 ºC and Load of 100 N (Experiment 7) Observed using SEM.

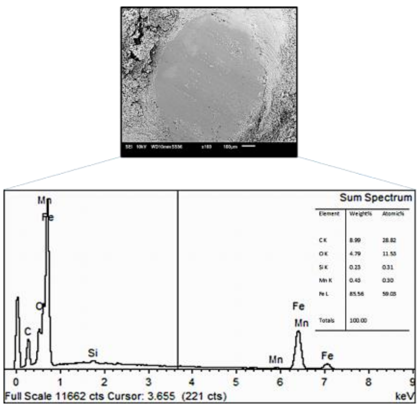

Figure 4.32b: SEM-EDX Images of Worn Surface of the Hemispherical Pin with Addition of 4.0% w/w of EC at 27 ºC and load of 100 N (Experiment 7) Observed using SEM.

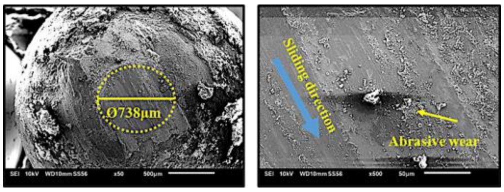

Figure 4.33a: Worm Surface and Wear Mechanism on the Hemispherical Pin with Addition of 0.5 % w/w of EVA at 27 ºC and Load of 60 N (Experiment 1) Observed using SEM.

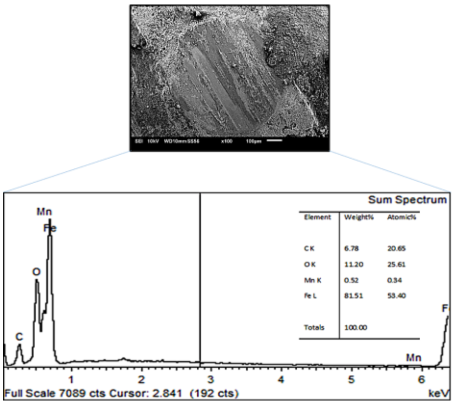

Figure 4.33b: SEM-EDX Images of Worn Surface of the Hemispherical Pin with Addition of 0.5 % w/w of EVA at 27 ºC and Load of 60 N (Experiment 1) Observed using SEM.

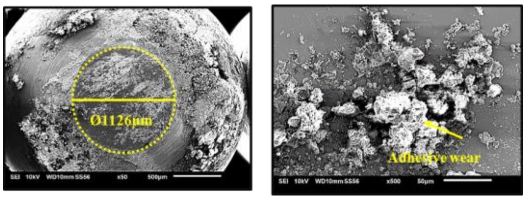

Figure 4.34a: Worm Surface and Wear Mechanism on the Hemispherical Pin with 0.5% w/w of EVA at of 27 ºC and Load of 100 N (Experiment 3) Observed using SEM.

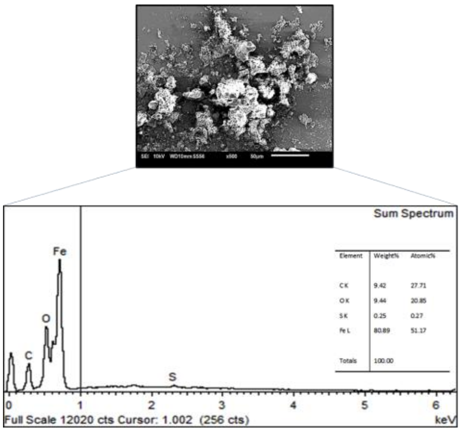

Figure 4.34b: EDX Images of Worn Surface of the Hemispherical Pin with Addition of 0.5% w/w of EVA at of 27 ºC and Load of 100 N (Experiment 3) Observed using SEM.

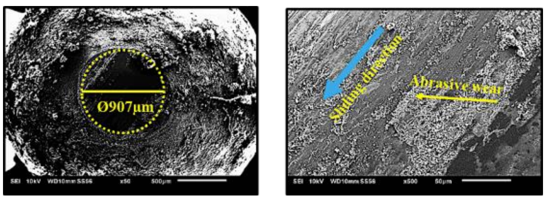

Figure 4.35a: Worm Surface and Wear Mechanism on the Hemispherical Pin with Addition of 4.0% w/w of EVA at 27 ºC and Load of 100 N (Experiment 7) Observed using SEM.

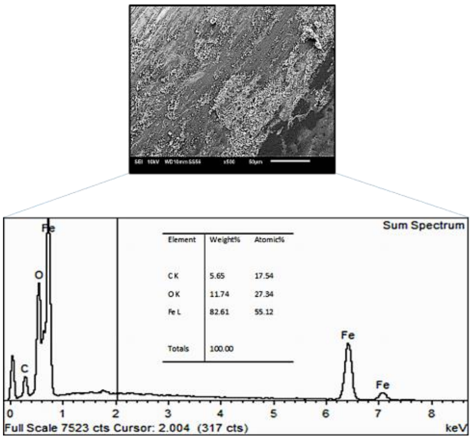

Figure 4.35b: EDX Images of Worn Surface of the Hemispherical Pin with Addition of 4.0% w/w of EVA at 27 ºC and Load of 100 N (Experiment 7) Observed using SEM.

4.0 Conclusion

Tribological investigation on the effects of biodegradable additives of EC and EVA on MBS oil at different strength of concentration were lead to the reduction of COF, WSD and Ws. Tribo-chemical reactions may occur between chemical composition of EC and EVA with fatty acids molecules in MBS oil which resulted in formation of protective tribo-chemical film. Predominant wear mechanisms of the particular oil were adhesive and abrasive wear. Further investigation on influenced factors, type of biodegradables additives and chemical interaction of the mixtures need to be done in order to understand the tribological regimes present in the tribo-chemical region.

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