lubricants

Article

Composite of Carboxymethyl Cellulose/MXene and Span 60 as Additives to Enhance Tribological Properties of Bio-Lubricants

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Abstract: Bio-lubricants are the future of lubricants as a substitute for mineral lubricants; however, bio-lubricants have drawbacks, such as poor thermal-oxidative stability. In addition, during the friction process, the temperature of the lubricant increases, so the lubricant must have good thermal conductivity to conduct heat to the environment. To combat the drawbacks of bio-lubricants, some additives have been used to improve their performance as lubricants. Composites of carboxymethyl cellulose (CMC)/MXene and Span 60 as surfactants were used as additives in CPO with different compositions. The physicochemical properties of the addition of CMC/MXene and Span 60 in CPO have changed, including kinematic viscosity, TAN, thermal conductivity, and fatty acids, which have a positive impact on lubrication performance in terms of reducing oxidation processes and increasing thermal conductivity. From fatty acid composition tests and FTIR analysis, the additives work to suppress the oxidation process. A pin-on-disk test was performed to evaluate the tribological performances of bio-lubricants. The results show that CM 10 SP (0.5% wt of CMC and MXene and 1% wt Span 60) demonstrated a significant decrease in CoF and wear rate by 49% and 74%, respectively, at a load of 50 N and a speed of 1400 rpm compared to CPO without additives. An interface layer of CMC/MXene and Span 60, separating two surfaces, could induce wear on the surface of the disk and pin.

Keywords: surfactant; wear; CoF; CPO

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1. Introduction

Bio-lubricants are future lubricants that will replace mineral and synthetic oils due to environmental concerns because they have some advantages, including being biodegradable and non-toxic [1]. Although mineral and synthetic oils have superior performance and are widely used as lubricants in the automotive industry, they are not environmentally friendly. Meanwhile, bio-based oil has good lubricant properties but has one disadvantage, which is low thermal-oxidative stability [2]. It contains unsaturated fatty acids that actively react with oxygen to form peroxides, which affect the viscosity and performance of the lubricant [3]. Therefore, bio-based oil is not widely used in industry. Many researchers are currently focusing on improving the weaknesses of bio-based oil so that it can be used in industry.

To improve thermal-oxidative stability in bio-based oils, a chemical modification process such as transesterification is used, which eliminates the hydrogen molecule at the beta carbon position by substituting glycerol with polyols that do not contain beta hydrogen [3]. Another way to eliminate the disadvantages of bio-based oils is by adding additives to improve their lubricant performances significantly [4]. Organic compounds [5], ionic liquids [6], and nanomaterials [7] have been adopted and studied as lubricant additives. Organic compounds are a form of oil additive that is environmentally friendly and improves not only the physical but also the tribological properties of lubricant oils [5]. Furthermore, ionic liquids not only enhance the inherent tribological performance of the lubricant bio-based oils but also enhance physiochemical properties and subdue undesirable properties [6]. Moreover, nanomaterials can significantly reduce wear and friction through self-repair and the formation of a lubricating film [7] due to their atomic size and surface effect.

Nowadays, due to the growing environmental and ecological concerns associated with using synthetic polymers, cellulose compounds are often used as additives in lubricant oils to increase the performance of lubricant oil [8]. Cellulose is an alluring material as a matrix and substrate for the preparation of multifunctional composites because of its convenient water processability, good biodegradability, mechanical strength, biocompatibility, natural abundance, and sustainability [9]. Carboxymethyl cellulose (CMC) is a cellulose derivative that is widely used in industry. CMC is a linear polysaccharide of anhydro-glucose that is used to enhance viscosity, control the rheology of a solution, avoid the separation of water from a suspension, and improve surface or barrier properties [8]. CMC acts both as a film-forming agent and as a stabilizer and emulsifier for an aqueous system. Research conducted by Opia et al. recently showed that adding CMC to rapeseed oil can reduce the friction coefficient and wear by 44.8% [10].

MXenes are a class of two-dimensional (2D) inorganic compounds notable for their distinctive physical and chemical properties that combine aspects of both metals and ceramics [11]. Due to the unique mechanical properties of MXenes, they have received extensive attention in the field of tribology as an additive [12]. As a result, MXenes have been revealed to be an excellent lubricant candidate due to their low friction and wear rate in various tribological applications [13]. The properties can be applied in tribology due to weak interlayer interactions and a highly specific surface, which makes them readily slide between interlayers under pressure and easily form lubrication [14,15]. Since MXenes were first discovered in 2011, their application has grown not only in liquid lubrication but also in solid lubrication. Some investigators [16–18] have demonstrated that the addition of MXenes enhances the tribological performance of the base oil, where, as an additive, MXenes contribute to the formation of a uniform and continuous tribofilm on the contact surface.

The potential problem of solid–liquid lubricants is agglomeration. It is associated with the high surface energy of nanoparticles and their ability to adsorb large amounts of oxygen, nitrogen, and moisture from the environment. To prevent agglomeration in liquid media, surfactants are used to stabilize the dispersion in lubricant for a long period of time [19]. The selection of an appropriate surfactant is crucial to achieving the desired friction-reduction and anti-wear properties. In several studies, surfactants have been known as anti-wear or anti-friction additives for their superior performance in lubricating oil, consisting of nano or colloidal particles [20].

The use of MXene/CMC as a water-based lubricant was investigated by Rahmadiawan et al., and the result shows that the addition of MXene and CMC with 0.4% and 0.7% wt, respectively, in water can decrease the coefficient of friction by around 25% compared to water [21]. In this study, crude palm oil (CPO), which grows in tropical countries like Indonesia, will be used as a lubricant base oil. This oil has good properties as a biobased lubricant because it has a high viscosity index, is a biodegradable lubricant, and has good lubricity [22–24]. However, this oil still has some drawbacks as a candidate bio-lubricant. Therefore, it is necessary to improve its physicochemical and tribological properties by adding some additives. In this research, a composite of CMC/MXene will be added as an additive to CPO to increase its performance as a bio-lubricant. To prevent agglomeration of the solution between MXene and CPO, Span 60 will be added as a surfactant in the solution. The characteristics of the physicochemical and tribological properties of the bio-lubricant will be investigated.

2. Materials and Methods

2.1. Materials

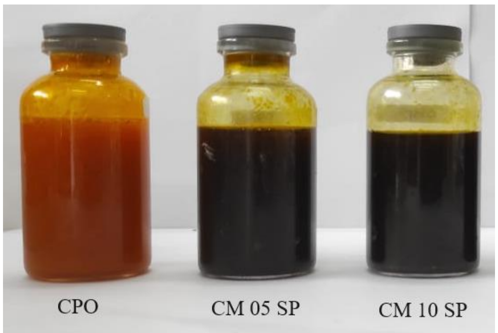
In this research, crude palm oil (CPO) was used as a biobase lubricant. The CPO was procured from small and medium enterprises in the city of Lampung, Indonesia. Carboxymethyl cellulose (CMC) was produced by Ashland (Warszawa, Poland). The titanium carbide MXene phase was purchased from CV. Inovasi Teknologi Nano in Medan, Indonesia. The SEM (particle size) of MXene was ±5 nm with molecular formula Ti3C2Tx, molecular weight 195.6 g/mol, XRD 2θ = 6.5°, and purity > 99%. The surfactant used in this study was Span 60, which was produced by Sigma Aldrich (St. Louis, MO, USA).

2.2. Sample Preparation of Bio-Lubricants

Surfactant (Span 60) was added to a base oil (CPO) and stirred for one hour at a temperature of 70 °C and a speed of 2600 rpm to form a CPO and Span 60 solution. Then, the solution was added to CMC and MXene sequentially, and each addition was stirred for one hour at a temperature of 70 °C and a speed of 2600 rpm, respectively. There were 3 sample oils, namely crude palm oil (CPO), CM O5 SP, and CM 10 SP. The composition of each additive is shown in Table 1, and photos of sample oils are shown in Figure 1.

Table 1. Samples of oils used in this study.

No.	Sample Oils	CPO (% wt)	CMC (% wt)	MXene (% wt)	Span 60 (% wt)
1.	CPO	100	0	0	0
2.	CM 05 SP	98	0.5	0.5	1
3.	CM 10 SP	96	1	1	2



(**a**) (**b**) (**c**)

Figure 1. The solution of sample oils on day 0. (**a**) Pure crude palm oil (CPO), (**b**) 98% wt of CPO with 0.5% wt of CMC and MXene, respectively, and 1% wt of Span 60 (CM 05 SP), and (**c**) 96% wt of CPO with 1% wt of CMC and MXene, respectively, and 2% wt of Span 60 (CM 10 SP).

2.3. Characterization of Biolubricants

2.3.1. Physicochemical and Fatty Acid Composition Tests

The determination of viscosity, density, pour point, flash point, total acid number, and total base number was carried out to obtain a physicochemical analysis of the sample oils. The ASTM D445-21e1 [25] method was used to measure the viscosity of the sample oils at temperatures of 100 °C, and the ASTM D4052-22 [26] method was used to measure the density of the oils by means of a density meter. Moreover, the ASTM D92-18 [27] and ASTM D97-17b (2022) [28] methods were used to measure flash point and pour point, respectively. Furthermore, the ASTM D2896-21 [29] and ASTM D664-18e2 [30] methods were utilized to obtain the total base number and the total acid number, respectively. Finally, Ce 1a-13 and Ce 2-66 of the AOCS (2017) method were used to determine the fatty acid composition of the sample oils modified, acid-catalyzed esterification, and transesterification of free fatty acids and glycerides, respectively.

2.3.2. Tribological Test

A pin-on-disk test apparatus was used to determine wear and friction. The test specimen consists of a 440C stainless steel pin with a 7.938 mm diameter and an AISI 1015 disk with a 160 mm diameter. The surface roughness of the disk was 0.8 µm Ra, and the surface hardness of the pin and the disk was 610 and 135 BHN, respectively. All tests were set at room temperature. The pin was mounted vertically in a steel vice such that its face would be pressed against a rotating disk. The holder, along with the pin, was positioned at a particular track diameter. A track radius of 50 mm was selected for this experiment and was kept constant for the entire observation. The test was conducted by dripping down a lubricant sample to rotate the top surface of the disk, and the pin was pressed with constant pressure against the rotated surface using flexible arms. The apparatus enabled us to determine the wear magnitude by calculating the volume of material lost as a result of rubbing against the flat face of a rotating disk. After completion of the test, the pin and disk were taken out from the observation area to be cleaned with alcohol and dried, and they were removed and replaced with new ones. The removed disk was then cleaned with alcohol and dried before being further weighed by a balance with a tolerance of 0.01 g to determine the mass loss due to wear. The difference in the mass measured before and after the test indicated the wear of the AISI 1015 disk. The ratio of mass loss to sliding distance was defined as the wear rate. The wear test was carried out by keeping the load, speed, and time at a constant value. The rotational speeds were 500 and 1400 rpm, and the test was conducted for 15 min for the measurement coefficient of friction and 60 min for the wear test. Furthermore, the coefficient of friction was determined from the ratio of frictional forces measured using a load cell attached to a flexible arm, and the loading forces were determined from the weight loaded on the pin. The friction coefficient was measured at the same time as the measurement of wear.

2.3.3. Surface Morphology Analysis

The surface morphology of the pin and disk was examined with an Olympus SZX 10 stereoscope (Olympus, Tokyo, Japan), which has a zoom range of 0.63–6.3×. The scar diameter of the pin and the scar diameter of the disk were measured by the microscope. The wear morphology of the disk was evaluated using SEM, S-3400N Hitachi, and EDX (Hitachi, Tokyo, Japan) to investigate the material composition in the wear area of the pin and disk.

2.3.4. Conductivity Thermal and Fourier Transform Infrared (FTIR) Analysis

The thermal conductivity of sample oils is measured by their ability to conduct heat. For this purpose, we used the thermal conductivity analyzer C-Therm type TCi (C-Therm Technologies Ltd., Fredericton, NB, Canada). The thermal conductivity of the sample oils was measured at around 21 °C. Fourier transform infrared spectroscopy was used to test the infrared spectra of sample oils of CPO with different compositions of additives. FTIR analysis used a thermoscientific Nicolet iS-10.

3. Results

3.1. Physicochemical Characterization and Fatty Acid Composition

3.1.1. Physicochemical Characterization

The results of the physicochemical analysis of sample oils (CPO, CM 05 SP, and CM 10 SP) can be seen in Table 2, which consists of viscosity at 100 °C, density at 15 °C, pour point, flash point, total acid number (TAN), and total base number (TBN). From Table 2, the effect of adding additives with different compositions in CPO did not increase viscosity and density significantly. In contrast, the TAN values decreased slightly with the increase in the composition of additives. Meanwhile, the effect of adding additives to CPO caused the values of pour point, flash point, and TBN to be erratic. The addition of CMC/MXene 0.5% wt and 1% wt Span 60 in CPO (CM 05 SP) had a positive influence on the density, pour point, and flash point of the bio-lubricant.

Table 2. Physicochemical properties of sample oils.

Parameter	CPO	CM 05 SP	CM 10 SP
Viscosity at 100 °C, cSt	7.879	7.982	8.101
Density at 15 °C, kg/L	0.920	0.917	0.925
Pour point, °C	+12	+3	+21
Flash point, °C	260	268	242
Total acid number (TAN), mg KOH/g	18.60	18.25	16.80
Total based number (TBN), mg KOH/g	0.13	0.09	0.3

3.1.2. Fatty Acid Composition

The fatty acid analysis of CPO with different additives is shown in Table 3. Palmitic acid C 16:0 and oleic acid C 18:1 were the main compositions of the lubricants, where they are saturated and unsaturated acids, respectively. The increase in the percentage of CMC/MXene and Span 60 in CPO increased the saturated fatty acids in CPO but decreased the unsaturated fatty acids. Therefore, the ratio between unsaturated and saturated acids in lubricant oils decreased with an increasing percentage of additives.

Table 3. Fatty acid composition of sample oils.

Fatty Acid Composition (%)	CPO	CM 05 SP	CM10 SP
Saturated fatty acids (%)	49.08	50.39	50.82
Caprylic acid C 8:0	0.01	0.01	0.01
Capric acid C 10:0	0.01	0.01	0.01
Lauric acid C 12:0	0.13	0.13	0.16
Myristic C 14:0	0.98	0.99	1.01
Palmitic acid C 16:0	43.23	44.07	44.22
Stearic acid C 18:0	4.27	4.72	4.96
Arachidic acid C 20:0	0.38	0.39	0.38
Behenic acid C 22:0	0.07	0.07	0.07
Unsaturated fatty acids (%)	50.93	49.62	49.17
Oleic acid C 18:1	40.57	39.19	39.34
Palmitoleic acid C 16:1	0.16	0.16	0.15
Linoleic acid C 18:2	9.70	9.76	9.20
Linolenic acid C 18:3	0.26	0.27	0.25
Gondoic acid C 20:1	0.15	0.15	0.15
Docosahexaenoic acid C 22:6	0.01	0.01	0.01
Nervonic acid C 24:1	0.08	0.08	0.07
Ratio unsaturated and saturated fatty acids (%)	1.04	0.98	0.97

3.2. Thermal Conductivity and Fourier Transform Infrared (FTIR) Analysis

The results of the thermal conductivity measurement for sample oils are shown in Table 4. For each sample, thermal conductivity measurements were repeated 10 times; the average value was calculated, and the standard deviation was 0.0 W/mK. From Table 4, the thermal conductivity of CPO was 0.160 W/mK at 21.49 °C. There was an effect of addition additives in CPO, where the effusivity and conductivity thermal of the sample oils increased by 6.25% at temperatures around 21 °C to 531 Ws^{-2}/m^2K and 0.170 W/mK, respectively. There was no effect of increasing the thermal conductivity by 1% wt of MXene in CPO. The thermal conductivity values of the oils in this study were found to be similar to those in the previous study [31].

Table 4. Thermal conductivity of lubricant samples.

No.	Lubricant	Effusitivity (Ws^{-2})/(m^2K)	Conductivity (W/mK)	Ambient Temperature (°C)	Delta Temperature (°C)
1.	CPO	522	0.160	21.49	1.54
2.	CM 05 SP	531	0.170	21.46	1.53
3.	CM 10 SP	531	0.170	21.86	1.53

The quality of lubricant oil depends on the degradation of lubricant oil while in use. The common sign of degradation of lubricant oil is increased oxidation due to reactions with oxygen in the environment. In the degradation process, the classes of dominant reactions are soot particles, carbonyl oxidation products, nitrogen oxidation products, sulfur oxidation products, and fuel residues [32]. To analyze lubricating oil samples, FTIR was used. The results of the FTIR spectra of the sample oils are shown in Figure 2. From the figure, the peaks were 2920, 2851, 1743, 1464, 1160, and 721 cm^{-1}, respectively. The main signals present in the FTIR functional group of CPO, CM 05 SP, and CM 10 SP are reported in Table 5. Special attention is given to the carbonyl compound with a wave number of 1000–1800 cm^{-1}. The feature centered around 1743 cm^{-1} indicates the presence of carbonyl ester in this event, and the intensity suggests the function is still preserved. After the addition of additives to CPO, we observed the effect of the composite of CMC/MXene and Span 60 in CPO on these bands, with a significant decrease in absorbance, as shown in Figure 2.

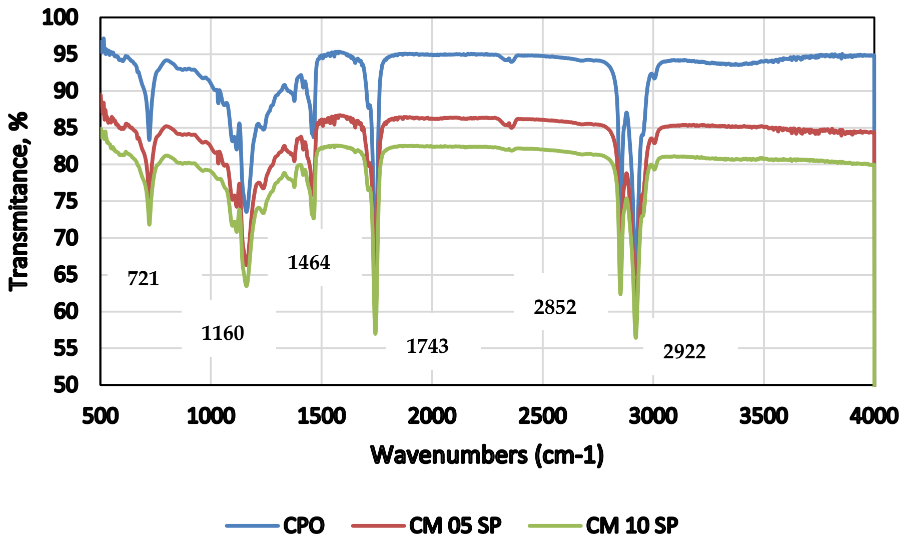


Figure 2. FTIR analysis of sample oils with different additives in CPO.

Table 5. Various significant FTIR functional groups (cm^{-1}) are present in CPO, CM 05 SP, and CM 10 SP, respectively.

CPO (cm^{-1})	CM 05 SP (cm^{-1})	CM 10 SP (cm^{-1})	Functional Group
721	721	721	C-H Group vibration
1160	1160	1160	C–O Stretching asymmetric
1464	1464	1464	C–H Scissoring and bending
1743	1743	1743	C=O Stretching vibration
2852, 2922	2852, 2922	2852, 2922	C-H Stretching vibration (aliphatic)

3.3. Coefficient of Friction (CoF)

The results of CoF measuring are shown in Figure 3, where tests were conducted at two rotational speeds of the disk, 500 rpm (Figure 3a) and 1400 rpm (Figure 3b), with a load of 50 N lubricated with different compositions of additives. The two rotational speeds represent different regime lubrications, which are boundary and mixed lubrications [33]. From Figure 3, it shows that at low speeds (i.e., 500 rpm), CoF values for different lubricants were higher than those at high speeds (i.e., 1400 rpm). This confirms that at low-speed regimes, the lubrication observed is boundary lubrication, with contact between asperity and asperity [33], whereas at high speed, the surface contact is separated by lubricant oil [33]. Therefore, CoF is increased at low speed and decreased at high speed. The effect of a composite of CMC/MXene and Span 60 in CPO for both speeds would decrease CoF, where base oil containing the MXene lubricant film has excellent friction-reducing properties. Additionally, it should be noted that the friction coefficient of CPO with any content of composite CMC/MXene and Span 60 is always lower than that of pure base oil (CPO) with different speeds. The CPO with 1.0% wt CMC and MXene and 2.0% wt Span 60 possesses the best tribological property at both speeds.

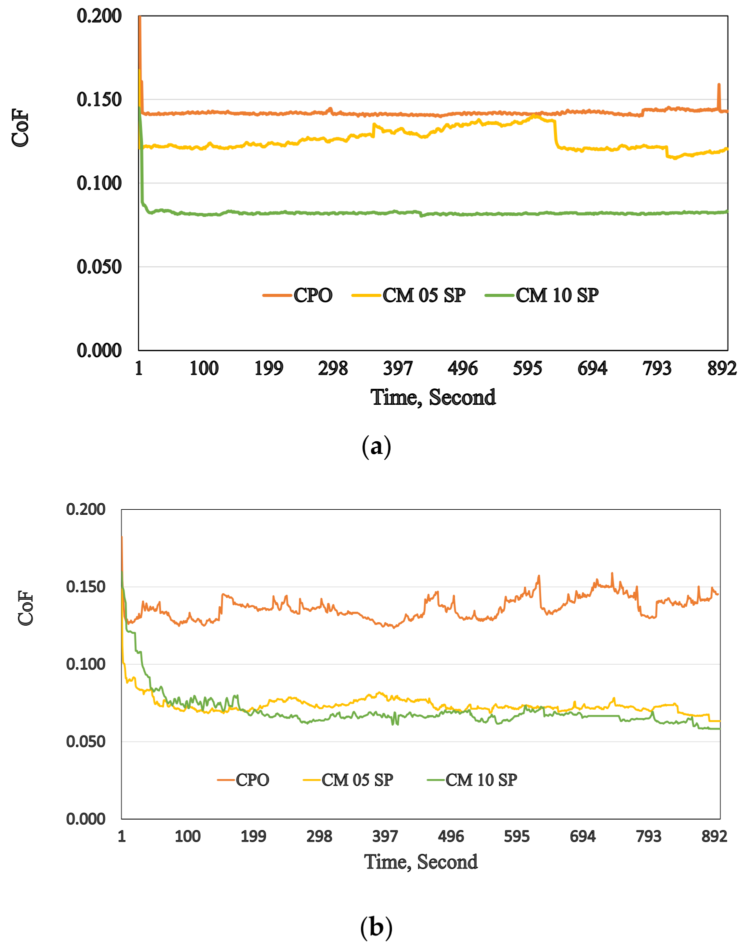


Figure 3. Comparison of CoF between speeds of (**a**) 500 rpm and (**b**) 1400 rpm with different additives of CPO at a load of 50 N.

3.4. Wear Rate

Wear mechanisms in sliding motion can include running-in, abrasive wear, adhesive wear, and delamination wear. In the absence of surface heating, friction tends to deform the contact surfaces, shearing them in the sliding direction and leading to material removal as wear particles. The wear behavior follows the Archad wear equation. The wear rate (k) was calculated using the Archad equation, where k is the comparison between the volume removed from the surface per unit sliding distance and the normal load applied to the surface by its counter body. Figure 4 depicts the results of the wear rate of disks calculated for different lubricants with a load of 50 N and a rotational speed of 1400 rpm for 60 min. The error bars show the standard deviation, indicating the experimental spread from the mean. The addition of a composite of CMC/MXene and Span 60 in CPO could reduce the wear rate of the disk, where the lowest wear rate of the disk was CM 10 SP. This may indicate a possible synergic action of the composite of CMC/MXene and Span 60. For CM 10 SP, the wear rate of the disk was reduced by 77%.

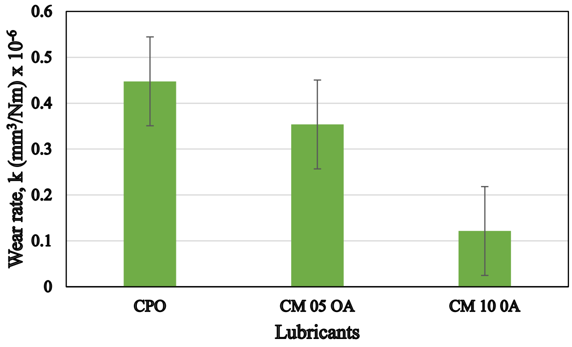


Figure 4. Wear rate of disks lubricated by different compositions of additives in CPO at a speed of 1400 rpm and a load of 50 N as a comparison CPO used.

3.5. Scar Width of Disk and Scar Diameter of Pin

The wear behavior of the pin-on-disk test was analyzed based on the wear scar width of the disk and the scar diameter of the pin. The volume lost is used in volumetric wear analysis. The wear volume is usually based on the wear scar length, depth, and width, but these parameters were difficult to measure accurately in this study. However, there are other methods that can be used to measure the wear volume by measuring it with a contact profilometer [34]. Therefore, the scar width and scar diameter were adopted as fair values to indicate the extent of wear on the disk and pin, respectively. The scar width of the disk and the scar diameter of the pin with different sample oils are shown in Figure 5. From the figure, the scar diameter of the pin was larger than the scar diameter of the disk for different lubricants. By increasing the concentration of the composite of CMC/MXene and Span 60 in CPO, the scar width and diameter of the disk and pin, respectively, dropped from a high value at the scar diameter and width of around 5500 and 3200 microns to a lower value at the scar diameter and width of around 3500 and 2200 microns for the pin and disk, respectively.

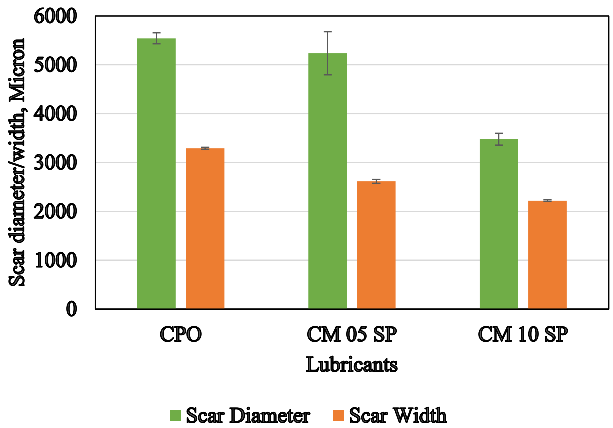


Figure 5. Comparison of the scar width of the disk and the scar diameter of the pin with different lubricants at a rotational speed of 1400 rpm with a load of 50 N.

3.6. Wear Surface Morphology and Chemical Analysis of Disk and Pin

The wear surface morphology of disks and pins lubricated by CPO with different compositions of additives with a load of 50 N and a rotational speed of 1400 rpm is shown in Figure 6. Chemical analysis of the wear track was carried out to show the presence of the element MXene on the wear surface of the disk and pin. This would infer the presence of a tribofilm composed of these additives in the contact. Tribochemistry plays a major role in understanding boundary lubrication, whereas tribophysics plays a major role in understanding elastohydrodynamic lubrication [33]. Under lubrication of CPO, the worn surface of the disk and pin is not only very rough but also characterized by serious plastic deformation and many signs of tearing (Figure 6a,d), which suggests that the disk and pin suffer serious wear. This agrees well with the results mentioned in Figures 4 and 5. With the addition of composites of CMC/MXene and Span 60 in CPO, the worn surfaces become smooth, and the plastic deformation is greatly abated. This indicates that the composite of CMC/MXene and Span 60 has good anti-friction properties. As the concentration of the composite of CMC/MXene and Span 60 increases, there are only some slight furrows on the worn disk surface (Figure 6c).

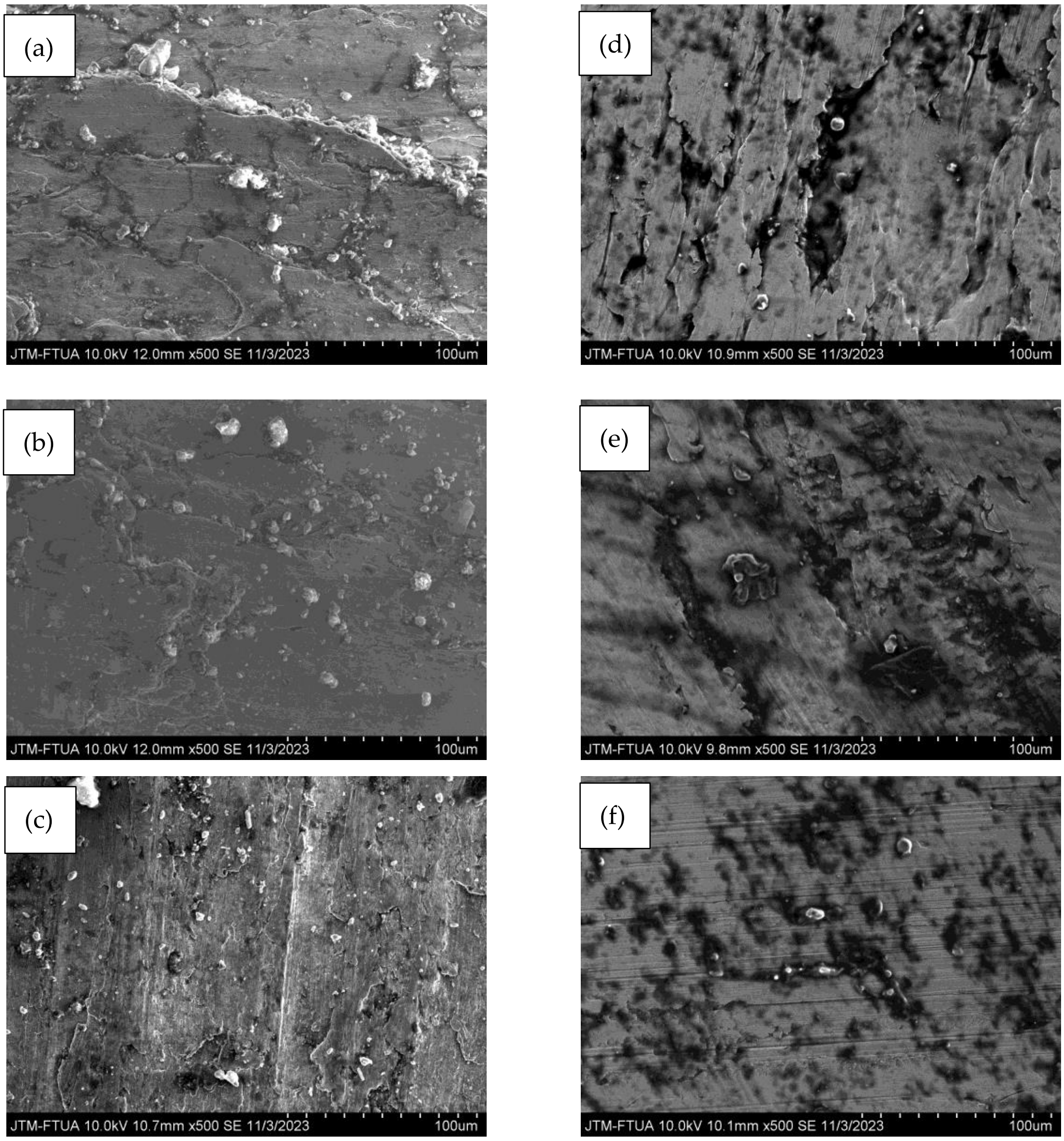


Figure 6. Wear surface morphology of disks lubricated by CPO with different additives (**a**) CPO, (**b**) CM 05 SP, and (**c**) CM 10 SP, and pins lubricated by CPO with different additives (**d**) CPO, (**e**) CM 05 SP, and (**f**) CM 10 SP with a load of 50 N and a rotational speed of 1400 rpm.

The tribofilm can be formed on the wear track through any one or more of these processes: tribo-sintering, chemical action, adhesion, absorption, or any other MXene lubrication mechanism. To better explain the tribological properties of the composite of CMC/MXene and Span 60, the corresponding element analysis of worn surfaces of disk and pin was performed (Tables 6 and 7). The tables show the SEM/EDX analysis of the chemical composition of the wear track of the disk and pin, respectively. Compared to Table 6, there are peaks of MXene elements appearing in Figure 6b,c, which are the EDX of the worn surface of a disk lubricated by CPO with 0.5% wt and 1.0% wt MXene, respectively. This is because during the friction and wear processes, MXene deposits on the worn surface under compressive stress to form a self-laminating film. However, this is not the case for the worn surface of the pin, where the material of the pin is harder than the disk, so no peaks of MXene element appear in Figure 6d,e on the surface of the pin (Table 7). Therefore, the lubricating oil of CPO with a composite of CMC/MXene and Span 60 has much better friction-reducing and anti-friction properties than that without a composite of CMC/MXene and Span 60. The results of the EDX analysis of the surface of the disk and pin are shown in Figure 7.

Table 6. SEM/EDX analysis of the chemical composition of the wear track of the disk with different additives in CPO and with a load of 50 N and a rotational speed of 1400 rpm.

Spectrum	Disk					
	CPO		CM 05 SP		CM 10 SP	
	Element	Weight, %	Element	Weight, %	Element	Weight, %
Spectrum 1	C, O, Fe	22, 7, 71	C, O, Ca	65, 29, 6	C, O, Fe	21, 6, 73
Spectrum 2	C, O, Fe	27, 7, 66	C, O, Ca	31, 29, 40	C, Fe	14, 86
Spectrum 3	C, O, Fe	22, 9, 69	O, Mg, Si	60, 16, 24	C, Fe	14, 86
Spectrum 4	C, O, Ca, Fe	20, 7, 3, 69	C, O, Fe	24, 9, 67	C, O, Ca	42, 45, 13
Spectrum 5	C, Fe	35, 65	C, O, Fe	24, 4, 72	C, O, Si, Ca	23, 25, 11, 41

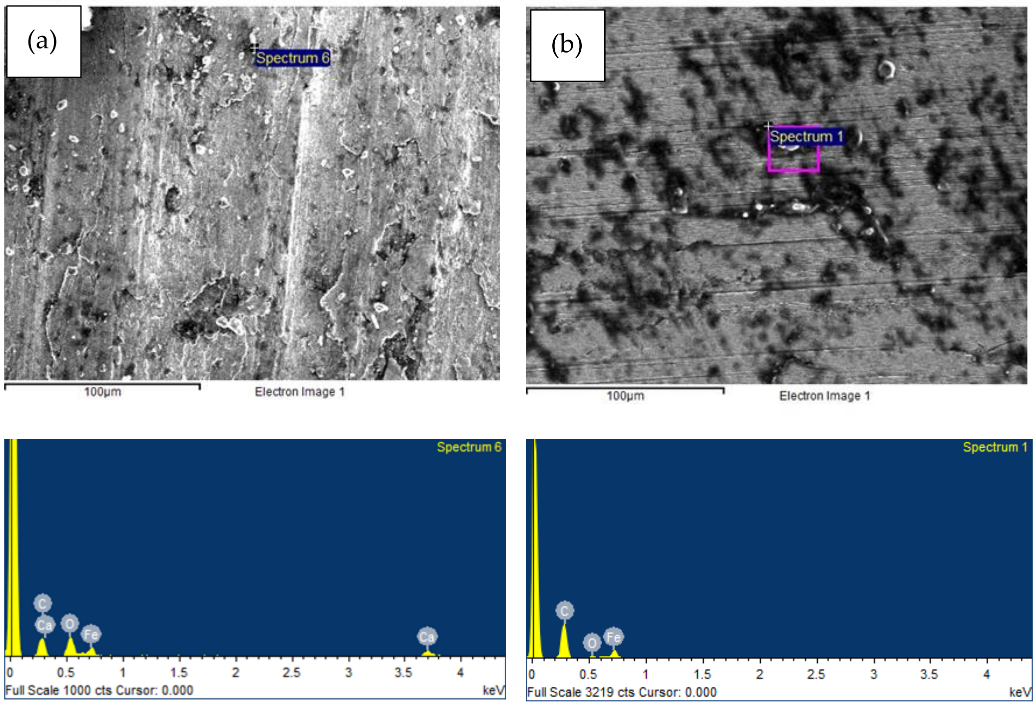


Figure 7. EDX analysis of the chemical composition of the wear track of the disk lubricated by CPO with different additives. (**a**) CM 10 SP (spectrum 6) and pins lubricated by CPO with different additives. (**b**) CM 10 SP (spectrum 1) with a load of 50 N and a rotational speed of 1400 rpm.

Table 7. SEM/EDX analysis of the chemical composition of the wear track of the pin with different additives in CPO.

Spectrum	Pin					
	CPO		CM 05 SP		CM 10 SP	
	Element	Weight, %	Element	Weight, %	Element	Weight, %
Spectrum 1	C, Fe	70, 30	C, O, Fe	51, 6, 43	C, O, Fe	53, 3, 44
Spectrum 2	C, O, Fe	30, 7, 66	C, O, Fe	57, 7, 36	C, O, Fe	29, 3, 65
Spectrum 3	C, Fe	21, 79	C, O, Fe	33, 5, 62	C, O, Fe	49, 3, 48
Spectrum 4	C, Fe	21, 79	C, Fe	37, 63	C, Fe	30, 70

4. Discussion

4.1. Physicochemical Properties and Fatty Acid Composition

The physicochemical properties and fatty acid composition of bio-lubricants were compiled in Tables 2 and 3. The most important physicochemical property of a bio-lubricant is its kinematic viscosity. The value found for CPO was 7.879 cSt, and by adding a concentration of CMC 1% wt in CPO, the kinematic viscosity of the lubricant increased to 8.101 cSt. The addition of CMC to CPO transformed the behavior of the lubricant from Newtonian to shear thinning. The increase in CMC in the lubricant was accompanied by a stronger time-dependence of the rheological properties [35]. From Table 5, the lowest total acid number (TAN) of bio-lubricant was found in sample oil CM 10 SP (16.80 mg KOH/g). It is evident that the composite of CMC/MXene and Span 60 could decrease TAN in the bio-lubricant. Table 3 shows that the addition of composites of CMC/MXene and Span 60 in CPO with different compositions could reduce the ratio percentage of unsaturated and saturated fatty acids. It indicates that the additives work by suppressing the oxidation process while in use. It is also supported by the FTIR investigation, where the peak of 1743 was a decrease in the absorbance of carbonyl ester. The conductivity thermal test performed shows that the addition of MXene to CPO increased the thermal conductivity of lubricants from 0.160 to 0.170 W/mK. There was no difference in the increasing thermal conductivity of lubricants with the addition of 0.5% wt and 1% wt MXene in CPO.

4.2. Tribological Properties

Figure 8 depicts the average CoF between the disk and pin lubricated by CPO with different additives. From Figure 2, the average of CoF decreased with the increase in speed and additive composition. An analysis of variance (one-way ANOVA) was used to compare the effects of composites of CMC/MXene and Span 60 with different compositions in CPO and speeds against CoF. The confidence level and p-value were 95% and 0.05, respectively. The results show that there was a significant effect (with a p-value < 0.05) of the composite of CMC/MXene and Span 60 against CoF at different speeds of 500 and 1400 rpm. Due to the significant effect of composites of CMC/MXene and Span 60 in CPO against CoF, one-way ANOVA post hoc tests were used to determine which compositions of composites of CMC/MXene and Span 60 in CPO differed. From the tests, there was a significant effect of CoF among compositions of composites of CMC/MXene and Span 60 in CPO for both speeds, 500 and 1400 rpm, with p-values smaller than 0.05. The decrease of CoF by adding composites of CMC/MXene with a percentage of 0.5% wt and Span 60 with a percentage of 1.0% wt in CPO was 49% and 42% for rotation speeds of 1400 and 500 rpm, respectively.

Tribo-improver, a composite of CMC/MXene and Span 60, can provide better lubrication performances synergically between wear and CoF. It indicates that the CoF, wear rate, and scar width and diameter of the disk and pin, respectively, had a significantly positive effect on performance lubrication. From chemical analysis using EDX, the chemical contents of MXene were found on the wear track of the disk in the form of Ca, Mg, and Si (Table 6). They indicate the formation of Ti3C2Tx tribofilm, which coated the tribocontact, generating low contact stress. Yang et al. [18] used 2D Ti_3C_2 as a lubrication additive in paraffin base oil, where the presence of Ti on the worn surface indicates the formation of

Ti_3C_2 tribofilm, which prevents direct contact between the friction pairs. In addition, the surfactant Span 60 was used to prevent the agglomeration of MXene in the solution of lubricating oil.

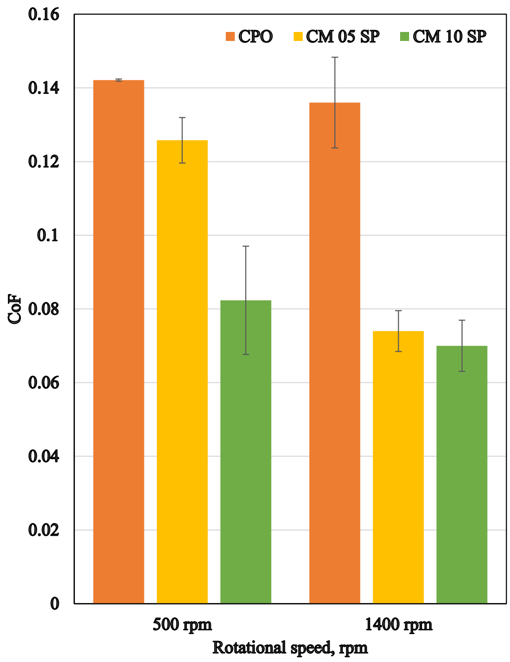


Figure 8. Average of CoF with different rotational speeds and compositions of additives in CPO.

In the friction process between two pairs of sliding contacted surfaces, the formed layer between the two contacted surfaces will determine the level of wear on the surface contacting bodies in relative motion. The interlayer of CMC/MXene and Span 60 could replace the relative sliding of two contacting surfaces and induce low wear. This is pointed out by the surface morphologies of the disk and pin in Figure 6, where the surface of the disk and pin lubricated with CPO without the addition of CMC/MXene and Span 60 was rough, and plastic deformation occurred on the disk surface. Moreover, composite CMC/MXene and Span 60 formed a lubricating film on the friction interface, which protects against severe wear on the disk and pin surfaces. Based on the theory of the mixed lubrication model, which was carried out by Gasni et al. [33], at 1400 rpm, the lubricant condition is in the mixed lubrication area, where the two contact surfaces are partly separated by contact between asperity and asperity and partly separated by the fluid layer. Therefore, physical and chemical properties play a major role in this regime. The addition of CMC to the lubricant can increase the viscosity of the lubricant [21], which is very good in this lubrication regime, as well as the addition of MXene, which is very good at protecting the two contact surfaces with low shear strength and weak interlaminar Van der Waals forces [36]. The composite between CMC/MXene and span 60 attributed the friction-reduction and anti-wear on performances to the adsorption of CMC/MXene and tribochemical reactions in the area of two contact surfaces.

5. Conclusions

The interaction of additives in base oils can result in a positive, negative, or neutral effect on lubricant performance, including its tribological and physicochemical properties. In this research, the addition of a composite of CMC/MXene and Span 60 with different concentrations in CPO increased the tribological and physicochemical properties of CPO. The physicochemical properties of addition additives in CPO changed, including kinematic viscosity, TAN, thermal conductivity, and fatty acids, which had a positive impact on lubrication performance in terms of reducing oxidation processes and increasing thermal conductivity. Tribo-improver of composites of CMC/MXene and Span 60 in CPO protected surface contact from wear and friction, where the CoF and wear rate were reduced by 49% and 70%, respectively, at a rotational speed of 1400 rpm. Meanwhile, composites of CMC/MXene and Span 60 as additives in CPO formed a surface layer coating the contact surface, which prevents direct contact between two rubbing surfaces.

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