5.4 Results and discussion

The results and discussion section has been divided into several section. The first section will be discussing about the effect of the size of GO flakes' size and pH regulation for friction coefficient and wear. The second section was the further observation on the addition of GO3 with the different pH level to different mating materials.

5.4.1 Size and pH level

The summarized results based on the regulation of GO dispersions size and pH level were dictated in Fig.5.6. These results were summarized from at least 3 data collection and were averaged to generate the comparison graph. From the results, the pH3 of GO1, GO2 and GO3 were clearly showed extremely low friction coefficient. The friction coefficients obtained were from the range of 0.05 for GO1 and GO2. Meanwhile, the friction coefficient of GO3 was still low in comparison to the overall GO dispersions' data. The depth and width of the wear track for all GO dispersion were almost the same in pH3. When dispersions were regulated to pH5, the friction coefficient increased slightly higher than 1. Further increment of pH values which were higher than pH7, the distinction of the tribological ability result was obvious. The tribological properties by GO1 started to deteriorate from pH7 where the friction coefficient exceeded 0.2 for pH7 and pH9 followed by as high as 0.55 for pH10 (this friction coefficient is similar to water lubrication without any additive [4]). On the other hand, the friction coefficients for GO2 and GO3 show the consistency until pH9. The friction coefficients at pH10 for both dispersions were around 0.25, lower than the result obtained by GO1. On the other hand, the correlation of the wear and the friction coefficient can be seen by the increment of depth and width of the wear tracks.

Fig.5.7, Fig.5.8 and Fig.5.9 were showing the micrograph images of the wear track of SUS304 flat plates and WC balls for all GO dispersion respectively. Started with Fig.5.7, as the results showed in Fig.5.6, pH3 and pH5 produced the lowest friction coefficient and also low wear on the contact surfaces. It was noticeable that both WC balls in Fig.5.7 only experienced small wear scar. On the other hand, pH 7 until pH 9

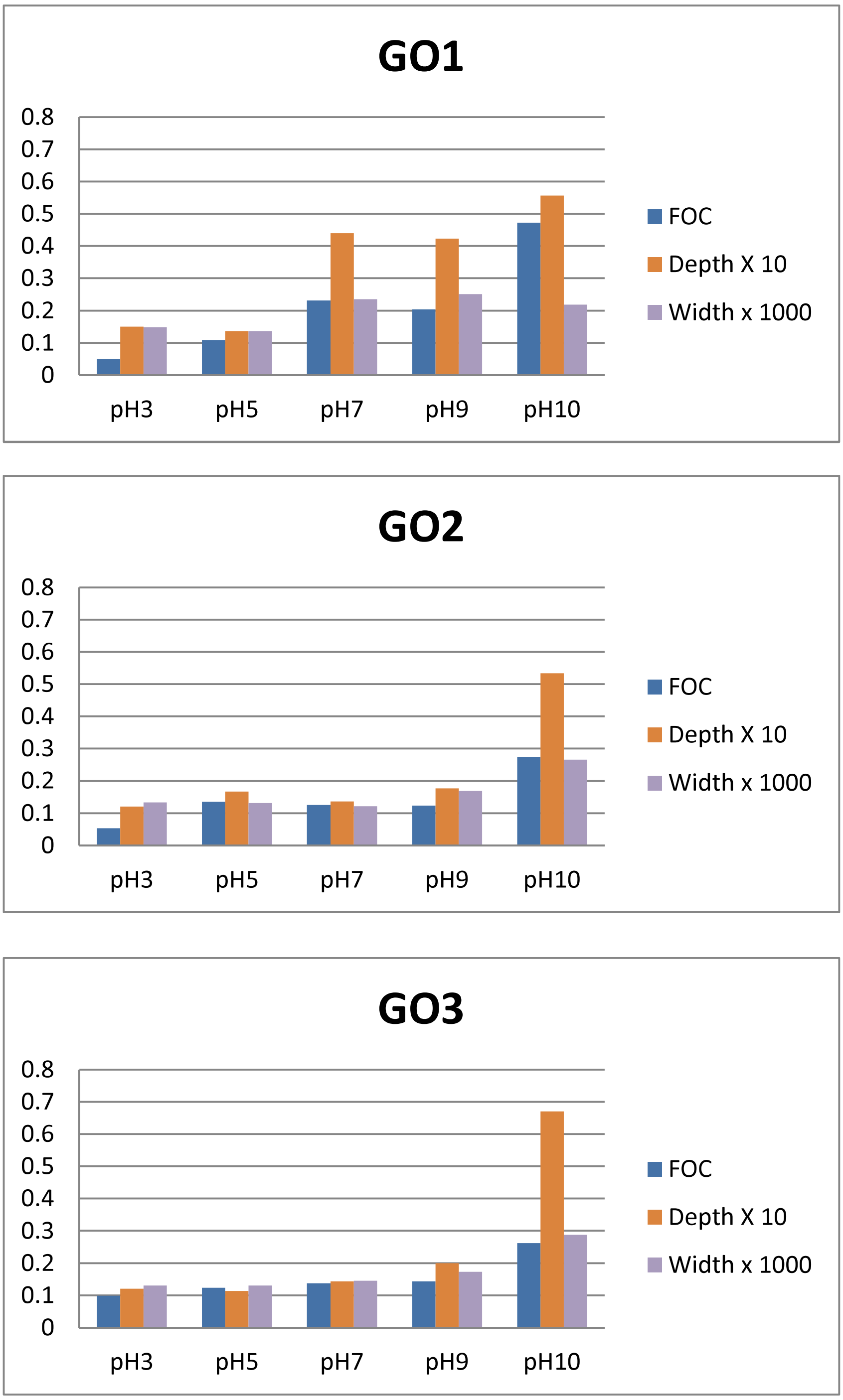

Fig.5.6 The summarized data obtained from acidity adjustment of different size of Graphene Oxides

showed larger wear scar. It was reflected to the wear track of SUS304. We can clearly see that the depth on wear tracks were obviously different for lower value of friction coefficients and higher friction coefficients.

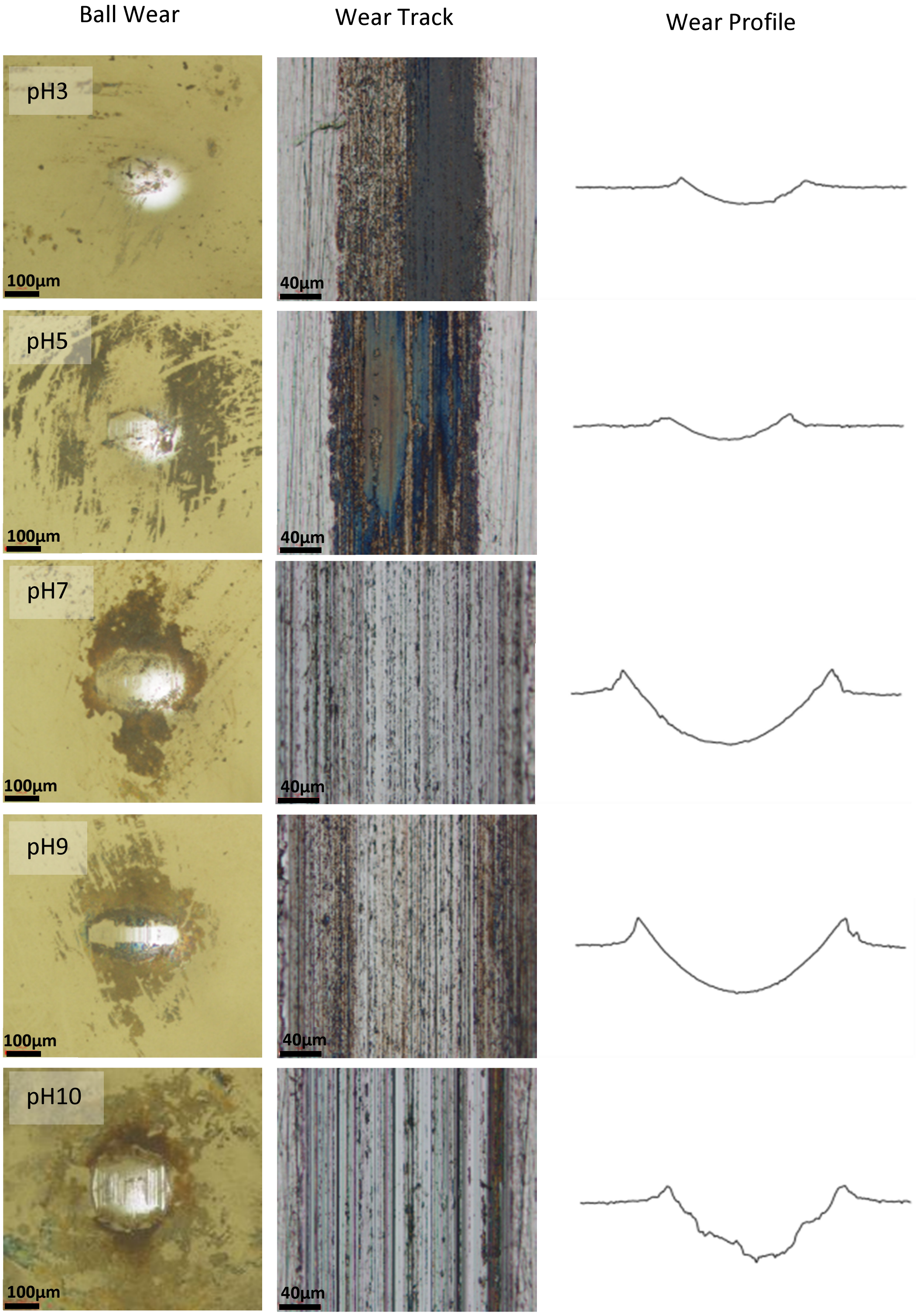

Fig.5.7 The microscopic images and depth profile of SUS304 substrates after the sliding test under GO1dispersions

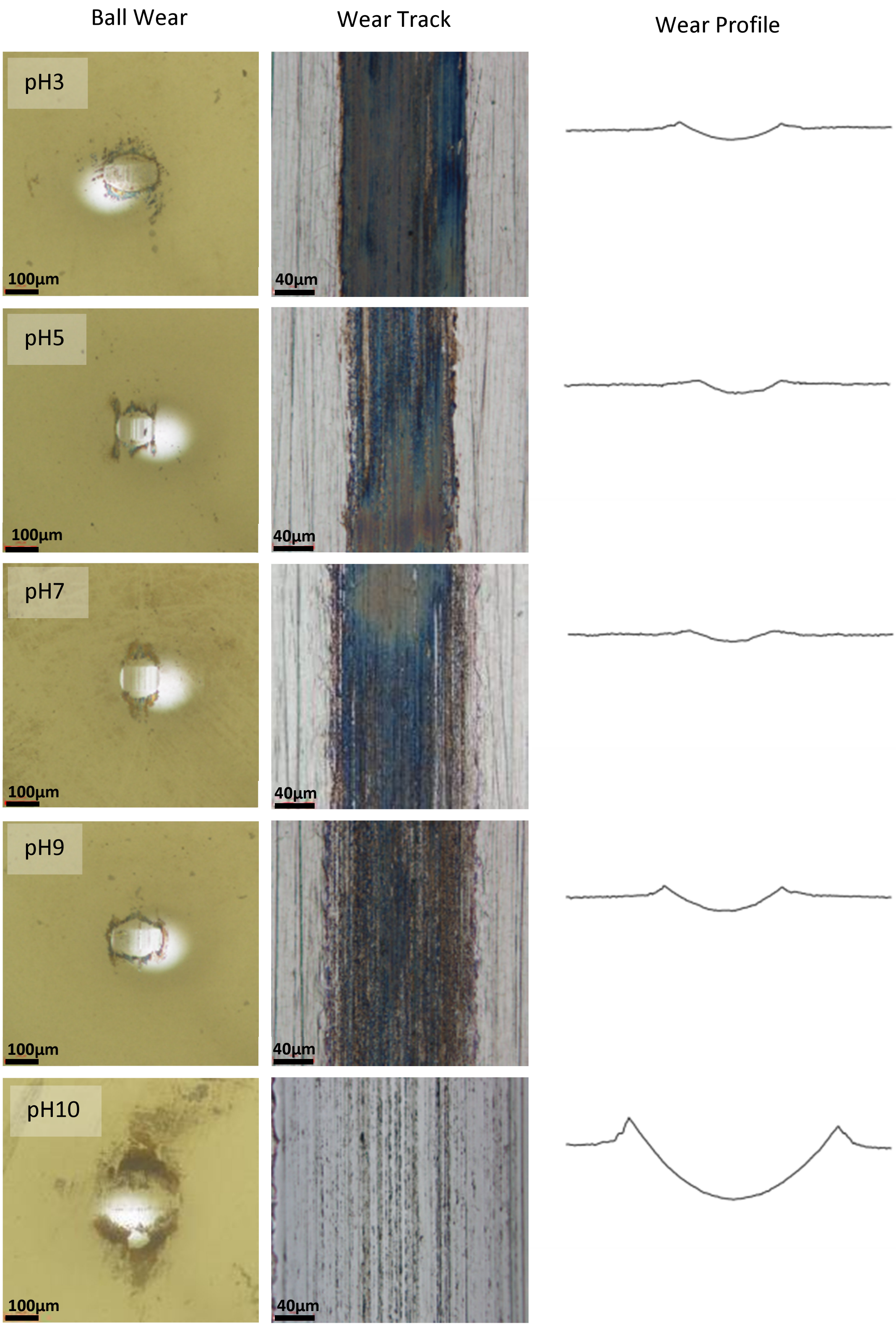

Fig.5.8 The microscopic images and depth profile of SUS304 substrates after the sliding test under GO2 dispersions

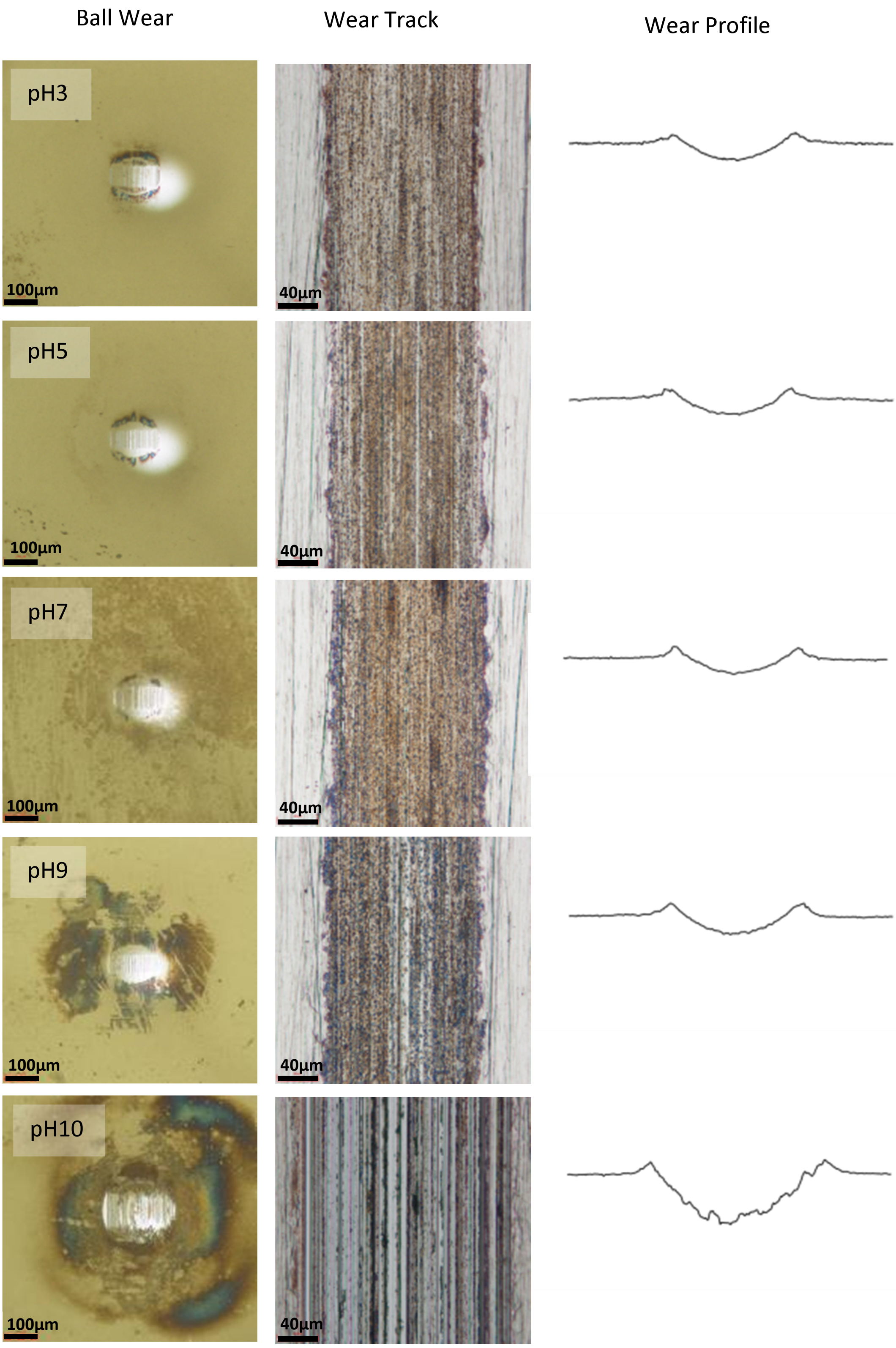

Fig.5.9 The microscopic images and depth profile of SUS304substrates after the sliding under GO3 dispersions

However, the most significant observation in the wear conditions was the tribofilms formation on the SUS304 flat plate. The wear track mainly covered by slightly dark tribofilm, and the friction coefficient was 0.1. This friction coefficient is as low as offered by conventional oil based lubricants. The similar tribofilms were not observed for higher friction coefficients, more than 0.2. The higher friction coefficient will leaved severe wear along the sliding direction of the wear track. Therefore, the tribofilms provided good tribological properties on the contact surfaces of the sliding materials. Moreover, it is clear that the formation of tribofilm is highly dependent on the pH level of the GO dispersion. The low pH levels will enhance the ability of GO to disperse in distilled water as shown in Fig.5.3, Fig.5.4 and Fig.5.5. As a result, the low pH levels will provide better GO dispersions by reducing the friction coefficient. However, instead of evenly dispersed in lower pH, the SEM images showed the accumulation of the GO flakes for pH10. This conglomerated of GO flakes inhibited the formation of tribofilms between the contact surfaces.

The observations on WC balls were also shown side by side of the wear tracks and wear side profile. The differences of the worn occurred on each ball surfaces were very clear. The formations of tribofilms on the wear track of GO dispersions obviously protected the balls from larger wear. On the other hand, severely wear on the ball by high friction coefficients of GO dispersion were found, which defined the poor tribological properties offered by the dispersion. Moreover, GO flakes substances seem to be adhered around the worn area of the ball shown by arrow in the image of the WC ball for pH10. The adherence of GO substances on the ball surface probably from the conglomerated GO flakes for higher friction coefficients. The similar formations of the substances were not observable around the wear areas on the ball for pH3 and pH7. It is because that there were only the evenly dispersed GO flakes for pH3 and pH7.

The formation of tribofilms was believed to be initiated by the adsorption of GO sheets to the flat plate substrates. This assumption is supported by the similar observation which has been done in a previous study on monolayer graphene oxide sheets [4]. This tribofilm was acting as a protective coating for the wear track. Hence reduce the friction coefficient at the same time govern the material from severe wear during the sliding contact. Moreover, the similar tribofilm was unable to be observed in the wear tracks of pH10 (GO1, GO2, GO3) and pH7 (GO1), where severely worn on the wear track were developed. The formation of GO tribofilm is highly dependent on the flake size of GO and the pH value of the GO dispersion. This is because sizes and pH values of GO are important in the ability of GO to be dispersed in water. Both size sand pH values are the main parameters in GO's amphiplicity where the ratio of hydrophilicity and hydrophobicity are important in providing dispersion ability of GO in water [5].

5.4.2 Materials Dependent

The studies on the different size of GO flakes in different level of pH conducted showed the best result in the original pH level. However, the observation only limited to the single type of mating materials, which were WC ball and SUS304 substrates. Therefore it is important to investigate the effect on other types of materials. For this particular test, only GO3 with pH3, pH7 and pH10 were used and compared to the result of distilled water.

5.4.2.1 Friction Coefficeints and Wear Condition

Similar to the previous section, the results also for this section also summarized into friction coefficients and wear formed in the test of various dispersions. Fig.10 shows the results from the combination of the similar mating materials, which is SUS304. The friction coefficient results show that pH3 able to reduce friction coefficient of distilled water from more than 0.6 down to as low as 0.25. However, this is not the best friction coefficient if compared to the WC ball against SUS304 flat plate. pH7 also shows a reduction in friction coefficient to 0.6. As expected, pH10 unable to provide better friction coefficient, similar to the previous section. Surprisingly, the wears of GO dispersions were worse than distilled water.

The microscopic images of the balls after the test show a variety especially the wear surface of ball under pH3. The condition of the surface around the wear was black and the GO sheets might be adhered to that particular area. The size of the ball's wear

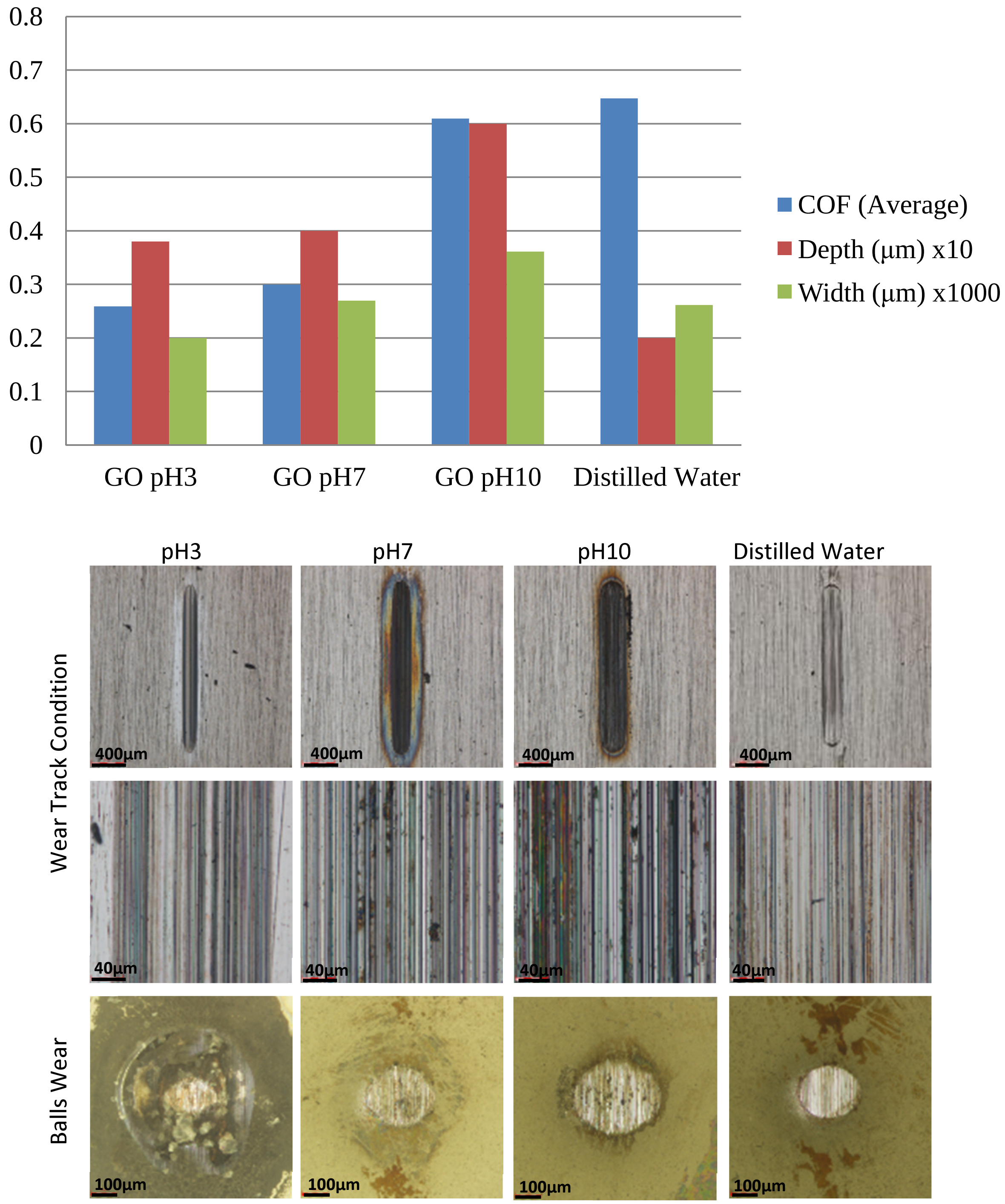

Fig.5.10 SUS304 ball vs SUS304 flat plate substrate

was also small. This was reflected to the width in the wear of pH3, as it was shown that the width was narrow. However, the depth was deeper than the one by distilled water. The observation on other wear tracks after the test in GO also gave similar results for the depth, which were deeper. Additionally, both of the wear tracks were also wider than pH3 and distilled water. The friction coefficient, width and depth of the wear tracks were correlated with the increasing of pH level. The GO dispersions however can only provide better friction coefficient for SUS304 ball and flat plate. Then, the similar tribofilm as explained previously cannot be observed.

The second types of materials combination were same as the previous section, WC ball and SUS304 flat plate. The results were also repeatability of the test with the addition of comparative result to distilled water. So, the results were the same where both pH3 and pH7 show very low friction coefficients. The depth and width were also small. The formations of tribofilms were detectable on both wear tracks. The pH10 of GO dispersion and distilled water show the same friction coefficient, which were near 0.5. However, similar to Fig.11 the wear depth and width of distilled water was better than pH10. Observation on the wear of ball and wear track also clearly show that the wear in pH10 GO dispersion was really poor. The conglomerated of GO flakes apparently gave poor tribological ability to water lubrication even for WC ball against SUS304 flat plate.

Lastly, Fig.5.12 shows the summarized results of the SiC ball, which is ceramic against SUS304 flat plate. SiC material alone known to possess high tribological functioning. Therefore, the friction coefficient in distilled water was really low in comparison to other mating materials. The friction coefficient by GO dispersions of pH3 and pH7 were higher than 0.1, which shown only little improvement. GO dispersion with pH10 however show higher friction coefficient than distilled water. The reason was similar as explained for WC ball against SUS304. However, GO dispersions show smaller effect on the wear effect. Although tribofilms seem to be formed on the wear track for the test in pH3 and pH7 of GO dispersions, pH10 of GO dispersion and distilled water also show black formation of substance on the wear track. However, the different of tribofilms formation indicates that the formation of tribfilm in distilled water and pH10 of GO dispersion might be dominated by the substance from SiC.

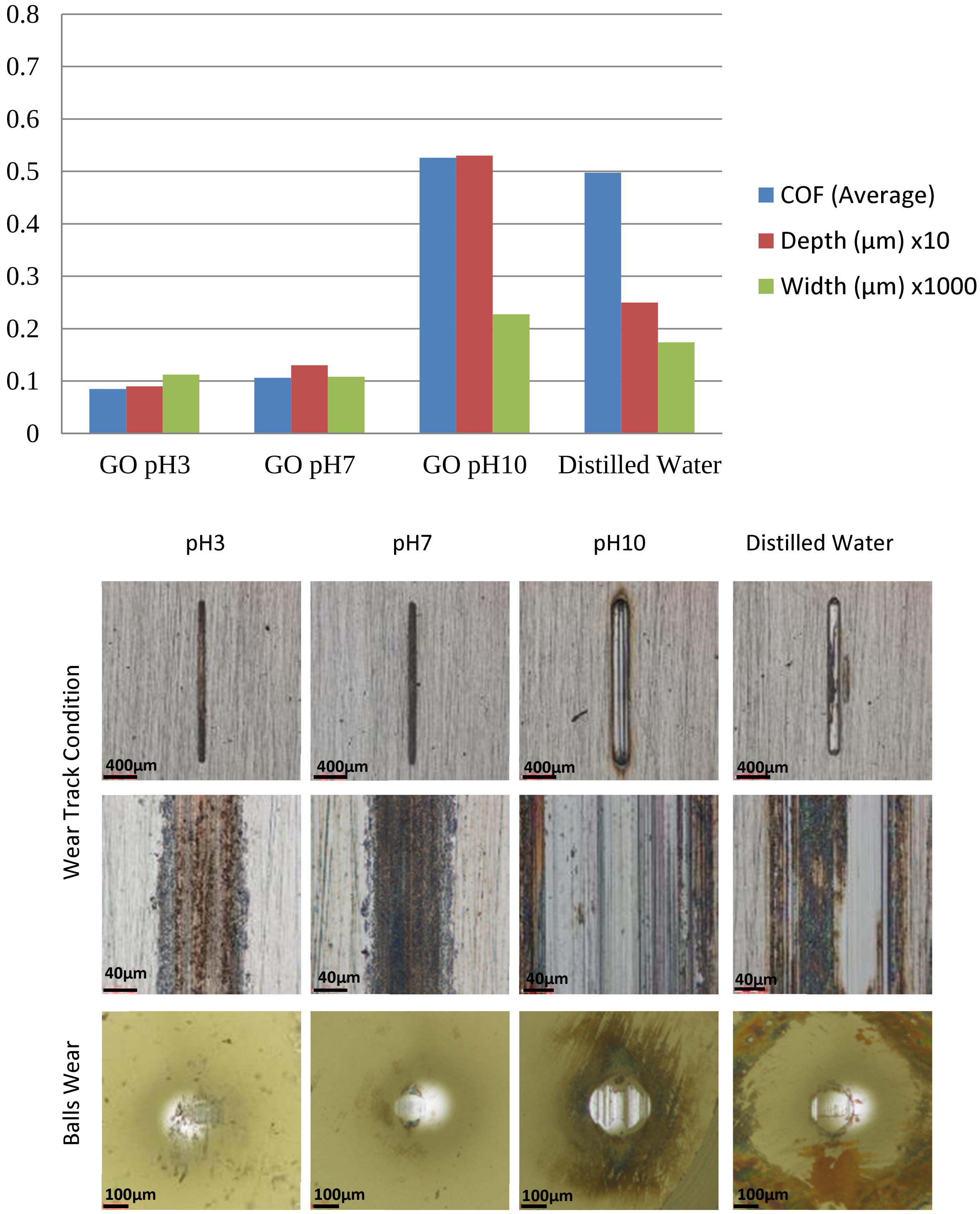

Fig.5.11 WC ball against SUS304 flat plate substrate

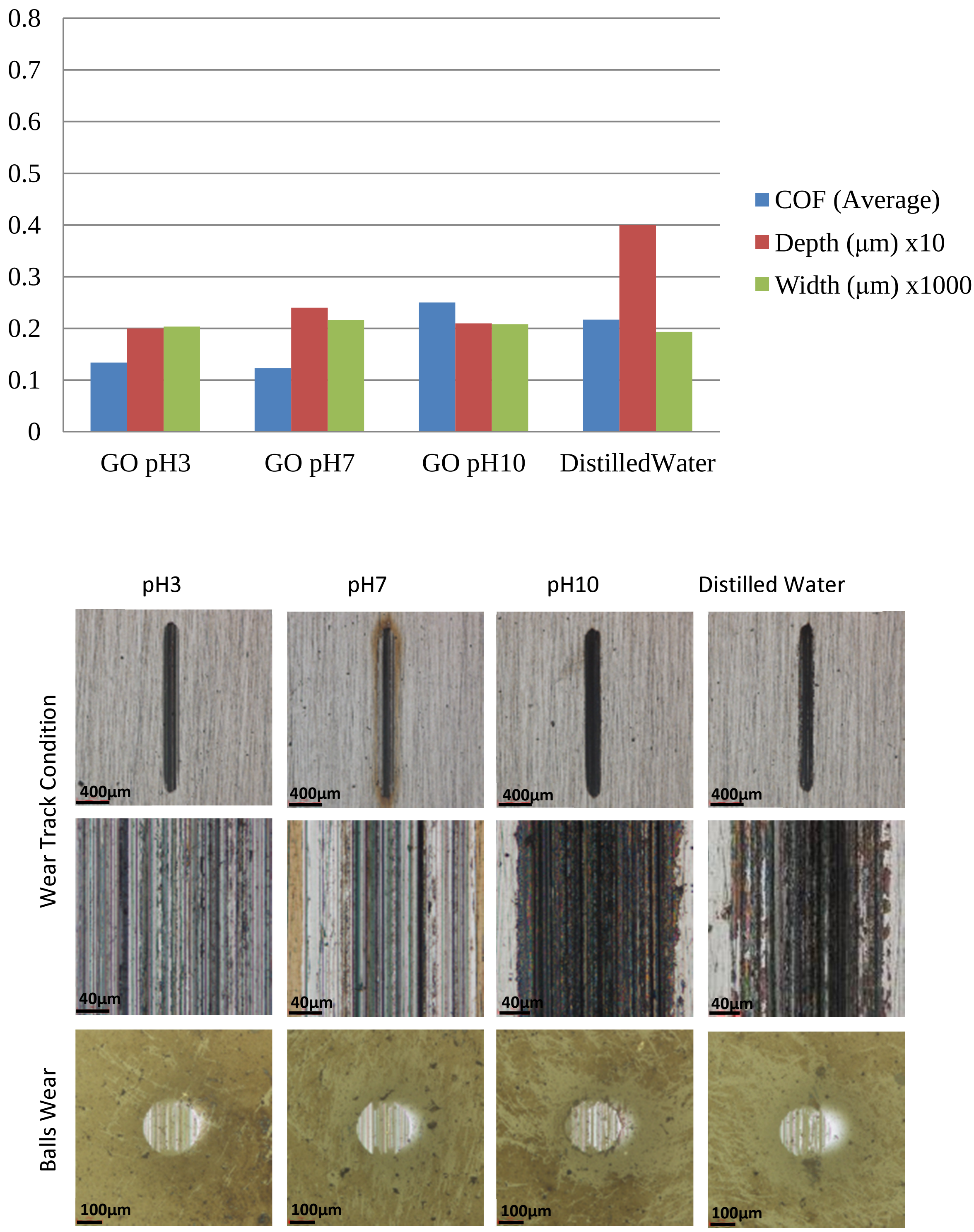

Fig.5.12 SiC ball against SUS304 flat plate substrate

5.4.2.2 Scanning Electron Microscope (SEM) observation and Energy Dispersive Spectroscopy (EDS) qualitative analysis

Further analysis on the formation of the wear track was carried out with the observation under SEM and EDS. These observations should be able to determine the materials composition on the wear tracks. Fig.5.13 shows the result obtained in distilled

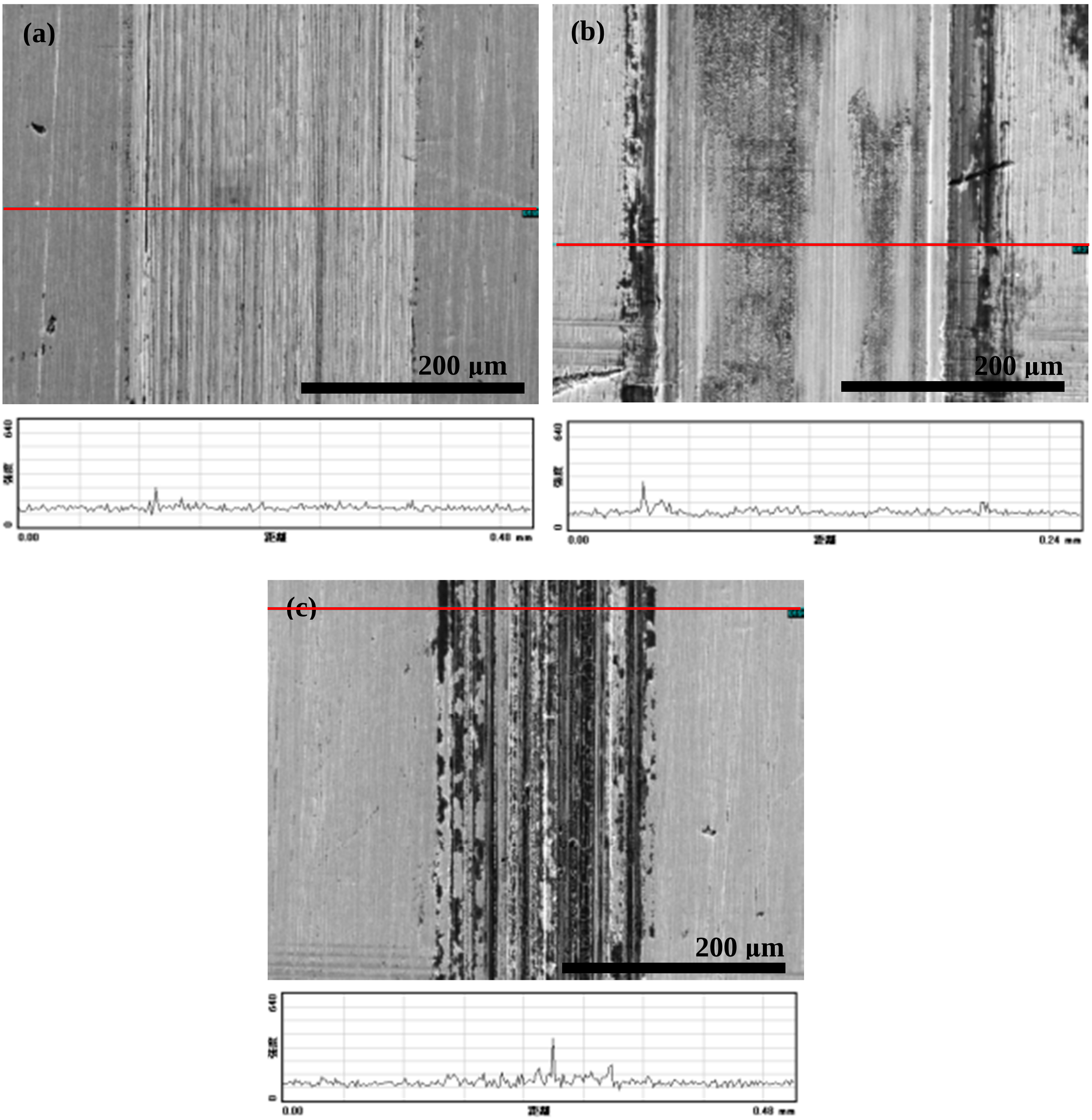

Fig.5.13 EDS analysis on SUS304 flat plate substrate against (a)SUS304, (b)WC and (c)SiC balls in distilled water

water. EDS was setup to analyse carbon composition and the comparison showing that black area contains carbon. However, the thick area along the transverse area crossed the wear track did not show any formation of the tribofilms.

An observation for the Fig.3.14 shows the appearance of carbon composition in (b) and (d). These observations were significantly determine the formation of GO tribofilms and supported by the results of friction coefficients obtained earlier.

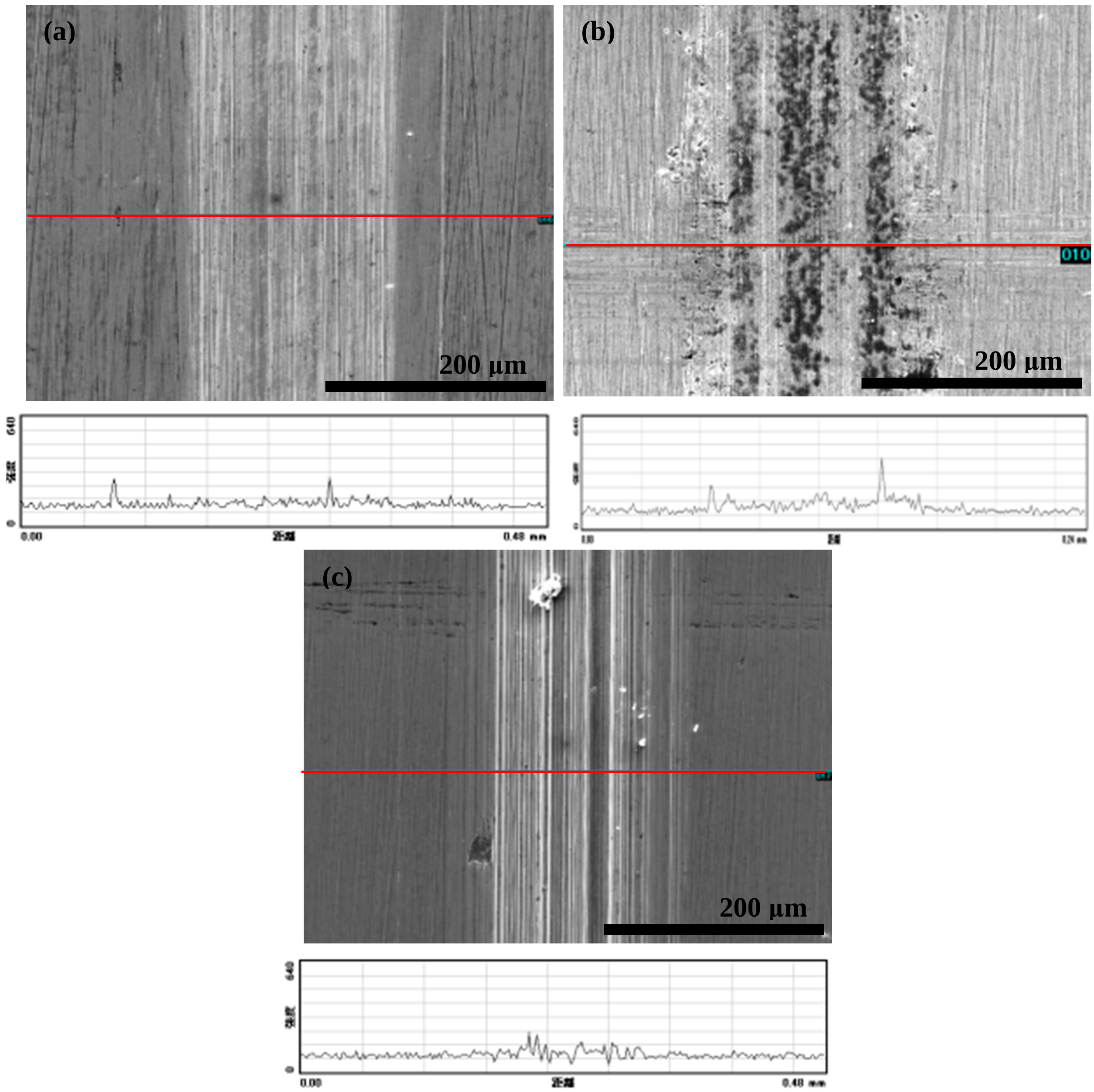

Fig.5.14 EDS analysis on SUS304 flat plate substrate against (a)SUS304, (b)WC and (c)SiC balls in pH3 GO dispersion

Fig.3.15 by pH7 of dispersions however show only small fraction of the carbon content. In (a), the carbon content seems higher outside the wear track rather than inside. Similar to Fig.5.14, the friction coefficient in SUS304 ball against SUS304 flat plate not significantly low indicates no possibility of the high functional GO tribofilms were formed. Both of (b) and (c9 show small fraction of carbon element in the wear tracks.

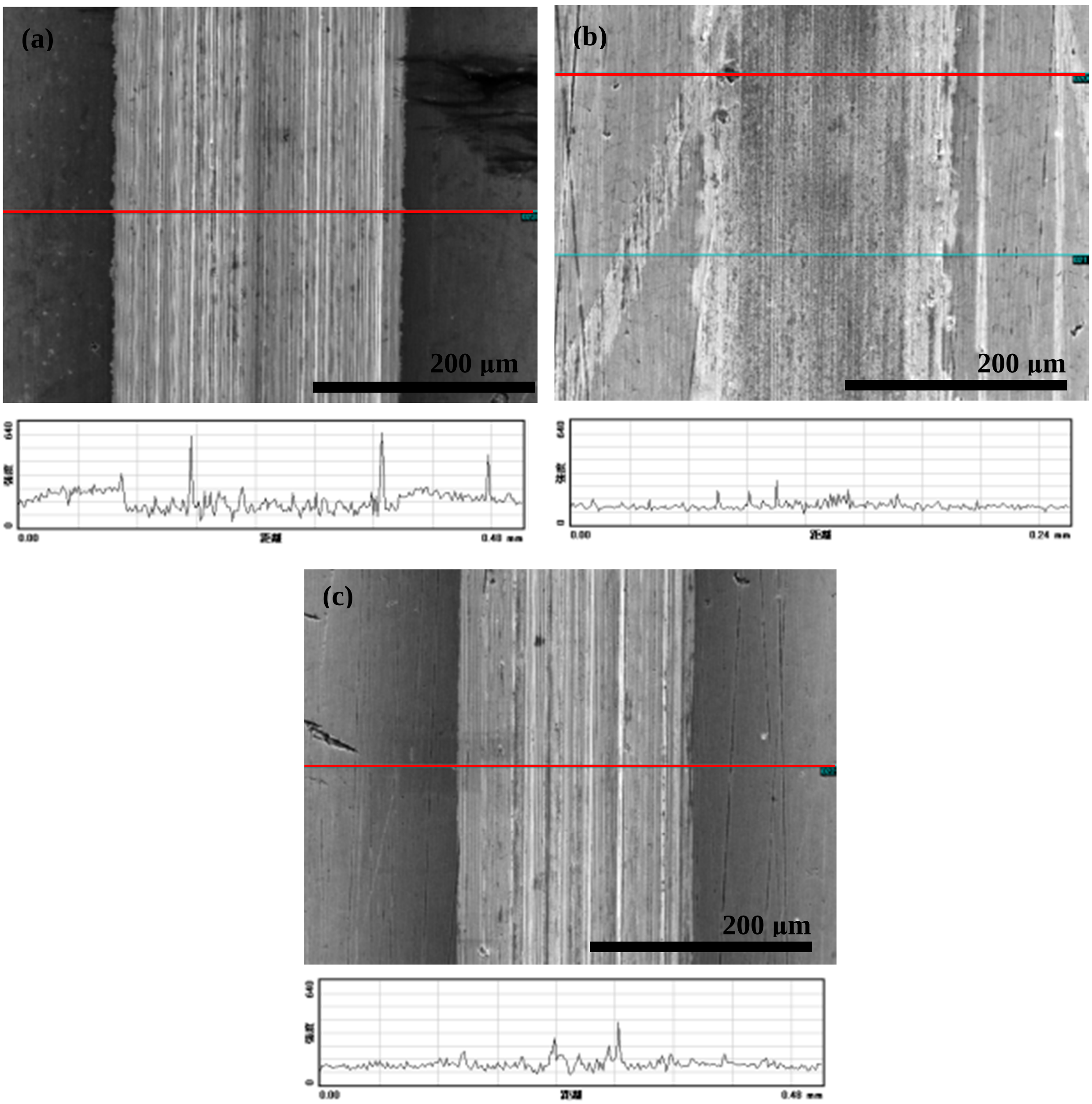

Fig.5.15 EDS analysis on SUS304 flat plate substrate against (a)SUS304, (b)WC and (c)SiC balls in pH7 GO dispersion

Lastly, EDS analysis on the wear track for the test under pH10 of GO dispersions. As predicted, no formation of GO tribofilms can be notice on both (a) and (b) in Fig.5.16 as the friction coefficients for both are high. Then in (c), the composition of carbon is clear. However, the formation of tribofilms might be from the SiC, not from the GO dispersion.

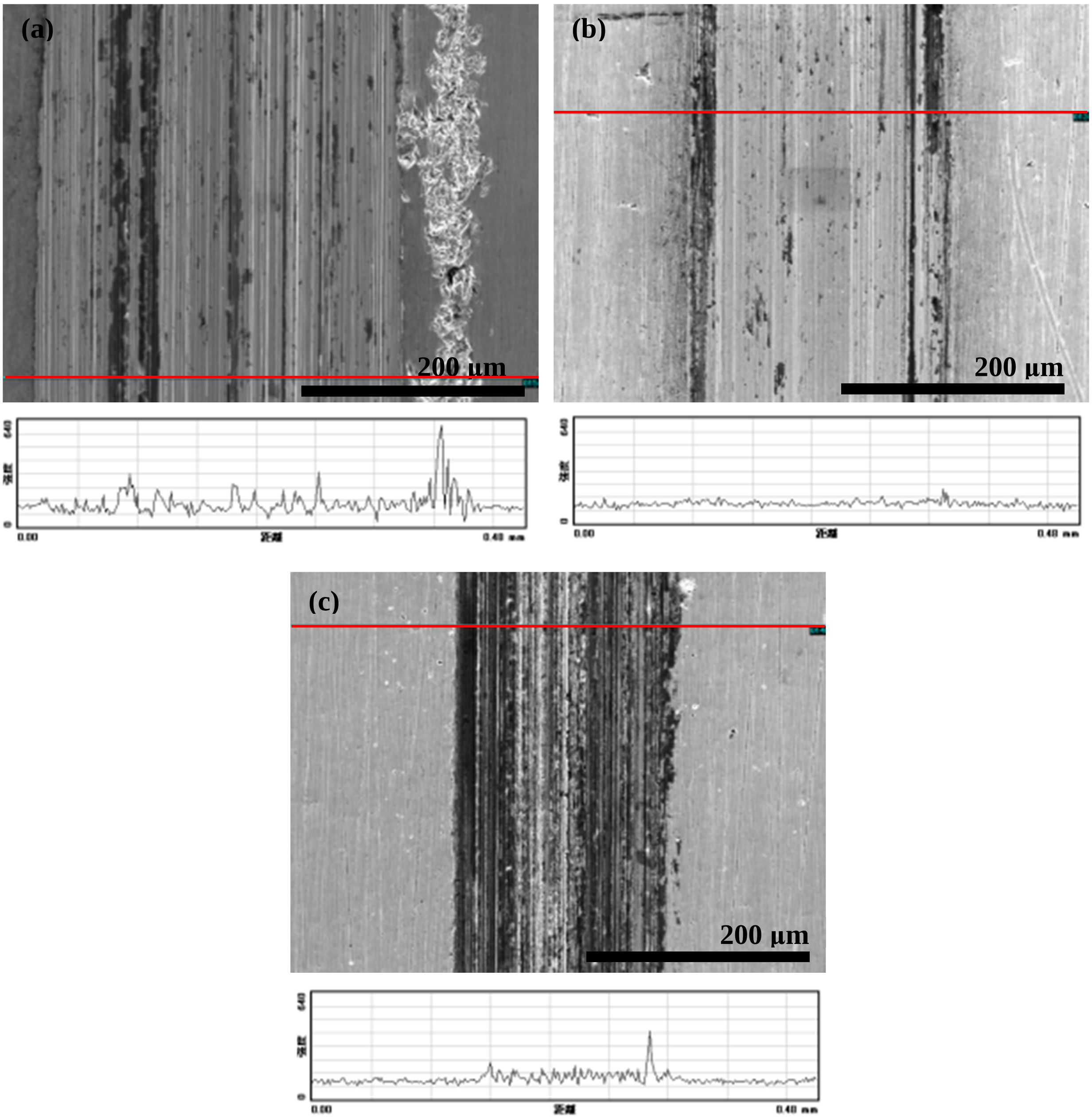

Fig.5.16 EDS analysis on SUS304 flat plate substrate against (a)SUS304, (b)WC and (c)SiC balls in pH10 GO dispersion

5.4.3 Centrifugation effect

The high friction coefficient resulted from pH10 of GO dispersions was probably originated from the amount of ion content in the dispersions after the pH level regulation process. Centrifugation procedure was executed in order to reduce the amount of ions in the GO dispersion. During the centrifugation process, GO flakes will be separated from the solution. The solution will be change to the new distilled water. It was carried out for several times until GO flakes not able to be separated with the solution.

Fig.5.17 shows the comparison of friction coefficient for the prepared GO dispersions for the test of WC ball against SUS304 flat plate. It is clear that the GO dispersion with pH10 produced high friction coefficient, which was slightly poorer than distilled water. Surprisingly, after the centrifugation process, the same dispersion was reduced the friction coefficient to 0.3, which was 50% from their original value. Therefore, it is clear that one of the reasons of conglomerated of GO flakes in pH10 was from the amount of ions in the dispersions. Ions possibly pull the GO flakes together, hence reduce the ability to provide frictional ability to the contact surfaces.

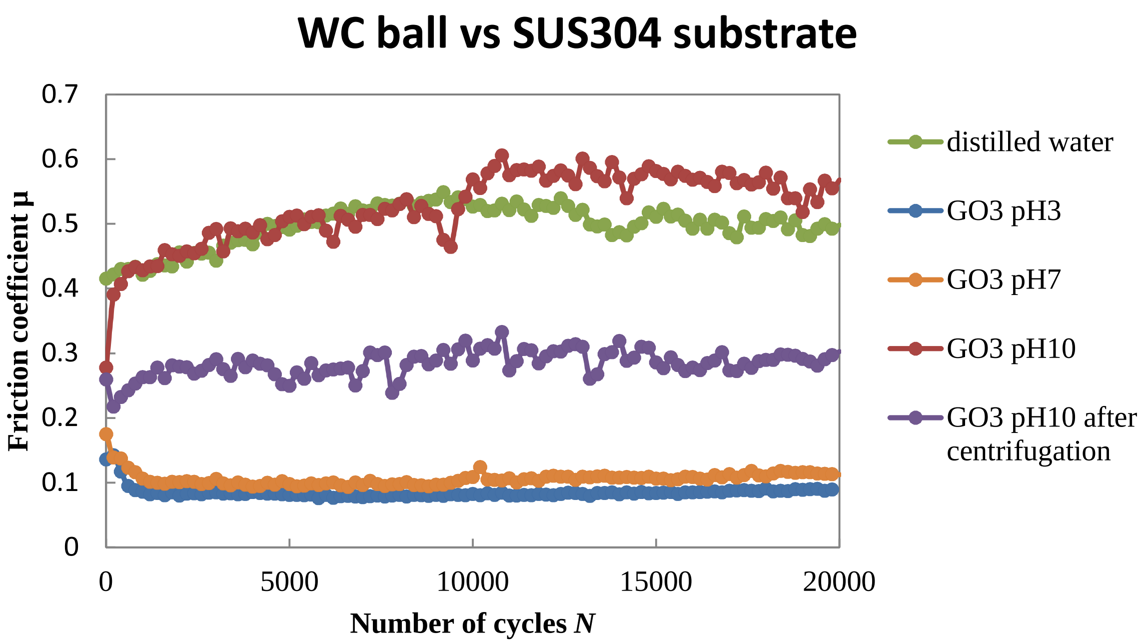

Fig.5.17 The summarized data obtained from acidity adjustment for WC balls against SUS304

5.5 Summary

The attributes of GO which is dynamic obviously effect the tribological properties of GO dispersions. The variation on the sizes and pH levels of GO dispersions were investigated by the friction sliding test. The configuration of pH level is important for the steel materials. In conjunction to the general study for this thesis, the experiments were carried out mainly on the WC ball and SUS340 flat plat. However, the effects of GO dispersions modification were done on other materials and parameters. The following are the summarize of this chapter;

1) The friction reductions and wear protection were highly dependent on the tribofilms formation on the contact surfaces. There were two types of tribofilms, dark black tribofilms able to reduce the friction coefficient down to 0.05. On the other hand, slightly dark tribofilms were only able to reduce the friction coefficients down around 1. However, both tribofilms were formed from GO absorbance on the contact surfaces.

2) The size of the GO flakes, which was also known as basal plane, is possible to be altered. The results obtained show that GO dispersions in different size able to provided low friction coefficients to the contact materials in their original state with pH3.

3) The increasing of pH level shows diversity in the results where the tribological properties of GO1 started to deteriorated at pH7. The increasing of pH level actually increases the amount of ion in the dispersion; hence reduce the tribofilm formation ability. The tribology properties of the smaller size of GO flakes, GO2 and GO3 were only deteriorated at pH10. It is because the smaller size of flakes is difficult to conglomerate between each other.

4) The formation of the GO tribofilms also depends to the type mating materials. In this study, WC ball against SUS304 flat plate experience the best tribological effect on friction coefficient and also wear. The same mating materials, SUS304 ball and

plate not able to get extremely low friction coefficeints. It is due to the adherence of the material between the surfaces. On the other hand, SiC ball does not reflected to the ability of GO dispersions in tribological properties.

Overall, further study need to be made in order to understand and define the quality of the tribofilms developed. The better tribological ability by GO also can be obtained by introduced longer structure of the carbon oxygen functional group.

References

[1] J. Lin, L. Wang, G. Chen, Modification of Graphene Platelets and their Tribological Properties as a Lubricant Additive, Tribol. Lett. 41 (2010) 209–215. doi:10.1007/s11249-010-9702-5.

[2] D. Berman, A. Erdemir, A. V Sumant, Few layer graphene to reduce wear and friction on sliding steel surfaces, Carbon N. Y. 54 (2012) 454–459. doi:10.1016/j.carbon.2012.11.061.

[3] Y. Liu, X. Wang, G. Pan, J. Luo, A comparative study between graphene oxide and diamond nanoparticles as water-based lubricating additives, Sci. China Technol. Sci. 56 (2012) 152–157. doi:10.1007/s11431-012-5026-z.

[4] H. Kinoshita, N. Yuta, A.A. Alias, M. Fujii, Properties of monolayer graphene oxide sheets as water-based lubricant additives, Carbon N. Y. 66 (2013) 720–723. doi:10.1016/j.carbon.2013.08.045.

[5] L.J. Cote, J. Kim, V.C. Tung, J. Luo, F. Kim, J. Huang, Graphene oxide as surfactant sheets *, Pure Appl. Chem. 83 (2010) 95–110. doi:10.1351/PAC-CON-10-10-25.

[6] U. Khan, A. O'Neill, H. Porwal, P. May, K. Nawaz, J.N. Coleman, Size selection of dispersed, exfoliated graphene flakes by controlled centrifugation, Carbon N. Y. 50 (2012) 470–475. doi:10.1016/j.carbon.2011.09.001.

[7] B. Konkena, S. Vasudevan, Understanding Aqueous Dispersibility of Graphene Oxide and Reduced Graphene Oxide through p K a Measurements, J. Phys. Chem. Lett. 3 (2012) 867–872. doi:10.1021/jz300236w.

Summary

This thesis describes the study on two types of nanocarbon materials, diamond nanoparticles (DNP) and Graphene Oxides (GO) dispersions as additives in water lubrications. The main objective of this investigation is to study the ability of both materials in providing water good tribological properties as a lubricant. Therefore it will increase several advantageous of water in replacing mineral oil as a lubricant for mechanical systems. It is important to have additives because water alone not able to deliver good lubrication ability to the contact surfaces. The results obtained in this thesis are summarized as listed below

(1) Both of the DNP and GO dispersions were able to reduce friction coefficients of distilled water as shown by the data obtained from the sliding friction test. In general, the obtained friction coefficients were as low as 0.1, which is similar to the friction coefficient by commercial mineral oil. In some conditions based on parameters selected, GO dispersions able to reduce the friction coefficient down to extremely low, 0.5. The friction coefficient obtained also highly dependent to the type of mating materials tested; in this thesis, WC ball and SUS304 flat plate combination shows the best results on both friction coefficient and wear. [chapter 3 and chapter 4]

(2) The friction coefficients obtained by the test under DNP dispersions can be divided into two running period, initial stage and steady-state stage. During the initial stage, the friction coefficient is high; the higher the concentration of DNP in water, the higher the value of friction force will be obtained. However, at the steady-state, the friction coefficient will be approximately the same. It caused by the embedded particles of nano diamond into the wear track of the flat plate, hence reduce the friction coefficient. Also in the steady-state stage, the wear of the ball seems to be increased. In addition, two type of wear on the flat plate and ball were observed. The

central striation which is clearly noticeable on wear track and lightly seen on the ball was formed during the high friction of initial stage. Furthermore, the wear was not really clear on the outer side of the central striation of the wear track. In contrast, the wear was clear on the surface contact of the ball. [chapter 3]

(3) The friction reduction by GO dispersions was promptly obtained after several sliding cycles. It was due to the formation of tribofilms on the contact surfaces. The tribofilm was formed by the absorbance of GO flakes onto the contact areas. This tribofilms were not only able to reduce the friction force, but also improve the wear of the materials due to the friction. The distinctions in the concentrations of GO dispersions were highly reflecting the friction coefficient. The higher amount of friction coefficient, which was 1 wt.% was shown the better result, followed by 0.1 wt.% and 0.01 wt.% of GO dispersions. It is clear that the dependent of tribofilm formation to the amount of GO. Here, an insufficient GO flakes were unable to form decent tribofilm. [chapter 4]

(4) Dynamics attributes of GO flakes were also highly influence the formation of tribofilm on the contact surfaces. In this thesis, dynamics attributes were measured by the modification of the size of GO flakes and the regulation of pH level of the GO dispersions. It is clear that the smaller the size of GO flakes, the easier GO flakes to be well dispersed in the water solution. Whereas, the higher pH level will reduce the acidity effect on the contact surfaces which commonly made from steel materials for mechanical systems. In this study, it has been confirmed that all sizes of GO flakes not able to provide good tribological ability for pH10. In pH10, the amount of ions were high; as a result, the GO flakes tend to agglutinate to each other. The amount of ions can be reduced by centrifugation, but not able to reach the lowest level of friction coefficients offered by the original GO dispersions in pH3. [chapter 5]

(5) There were two types of tribofilms formed on the wear track by GO dispersions. The first one was solid black, while the latter was light black. We observed the mixed tribofilms in some of the results. The appearance of solid black tribofilms

showed a reduction of friction coefficient down to 0.05 even though with the mixed formation with light black tribofilms. On the other hand, light black tribofilm alone was only able to reduce the friction coefficient down to 0.1. The friction coefficient of 0.1 can be considered very low for the lubricant. Therefore, from the study, it is believed that the GO flakes will filled the asperities at first before GO form light spotted black tribofilms. Then the best condition of the GO dispersions will assemble the smooth solid thin film onto the light black tribofilms. [chapter 5]

In general, GO dispersions able to provide better tribological properties to the mating materials compared to DNP. However, further evaluation on the quality of the formed tribofilms need to be done. In addition, the modification of GO flakes can be done by the addition of longer chain on their carbon oxygen functional groups.

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"In the name of Allah, the Most Gracious, the Most Merciful"

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