Vol. 36, No. 2 (2014) 163-171

Tribology in Industry

www.tribology.fink.rs

RESEARCH

Tribological Performance of Hydrogenated Amorphous Carbon (a-C: H) DLC Coating when Lubricated with Biodegradable Vegetal Canola Oil

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Keywords:

DLC coating
Biolubricant
Wear
Friction
Graphitization

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A B S T R A C T

Increasing environmental awareness and demands for lowering energy consumptions are strong driving forces behind the development of the vehicles of tomorrow. Without the advances of lubricant chemistry and adequate lubricant formulation, expansion of modern engines would not have been possible. Considering environmental awareness factors as compared to mineral oils, vegetal oil based biolubricants are renewable, biodegradable, non-toxic and have a least amount of greenhouse gases. Furthermore, improvement in engine performance and transmission components, which were impossible to achieve by applying only lubricants design, is now possible through diamond like carbon (DLC) coatings. DLC coatings exhibit brilliant tribological properties, such as good wear resistance and low friction. In this regard, tribological performance of a-C: H DLC coating when lubricated with Canola vegetal oil has been investigated by the help of a ball-on-flat geometry. Experimental results demonstrated that the a-C: H DLC coating exhibited better performance with Canola oil in terms of friction and wear as compared to the uncoated materials. Large amount of polar components in the Canola oil significantly improved the tribological properties of the a-C:H coating. Thus, usage of a-C: H DLC coating with Canola oil in the long run may have a positive impact on engine life.

1. INTRODUCTION

Considering the large number of vehicles in the world, an improvement of only a few percent of vehicles could have a large impact on energy consumption and emissions. For current scenario of automotive industry, there is a great deal of interest in improving environmental friendliness, reliability, durability and energetic efficiency. The reduction of wear and friction is a key element in decreasing the energy losses, particularly in engines and drive trains. Surface treatments and coatings contribute to a better lubrication with oils and can significantly participate in achieving these goals. Last two decades, significant researches on development and understanding of DLC coating have made it one of the promising coating processes. Their main advantages are good anti-wear properties, low friction, extreme hardness, adhesive protection and excellent corrosion resistance [1-8]. It has already proved its potential prospects in different machine component applications [9-12]. It reduces the wear rates and the values for coefficient of friction are low as it generates a transfer layer on the counter surface, which forms a tribo-film with lubricants.

Since increased awareness of environmental pollution and detrimental effect on human lives are of great interest, vegetal oil based bio-lubricants are getting popular as a substitute of conventional lubricants. They have potential sources, including lower toxicity, high viscosity index, good lubricating properties, and increased equipment service life, high load carrying abilities, good anti-wear character and rapid biodegradability [13-15]. Large amount of unsaturated and polar components of vegetal oil based bio-lubricant can promote the lubricity by generating lubricating film in the presence of coatings.

For the automobile components, which are operated under lubricated conditions, the failures and wear are predominantly linked to operation in the boundary lubrication regime [16]. In recent years, researches are carried on various types of biodegradable oils with DLC coatings [17,18], in tribological studies and field test with real mechanical components [18]. For vast application in automobile industry, further improvement of DLC coating with biodegradable oils is necessary. In this regard, the main objective of this experiment is to provide information to engineers, policy makers, industrialists and researchers, interested in DLC coatings with bio-lubricants for automotive applications. This study may support the establishment and encourage the research on DLC coating, combined with renewable natural sources as alternative lubricants. This current investigation presents the tribological behavior and compatibility of hydrogenated amorphous carbon (a-C: H) DLC coating with Canola oil. The tribology test has been conducted on a ball-on-flat contact geometry, in reciprocating sliding motion. Three different types of material combinations, such as steel/steel, steel/a-C: H and a-C: H/a-C: H, were used in this current investigation.

2. EXPERIMENTAL DETAILS

There are four main types of materials, which are used to make automotive components i.e. copper, aluminium, stainless steel and elastomers. This study only concerned with most friction prone area of engine, like piston ring, which is generally made by stainless steel. Test balls and disc were both made from 440C stainless steel. They exhibit similar mechanical, thermal and surface characteristics. Some of the steel samples were used as specimens in the tribological tests, while a deposition technique was used to coat the rest of discs and balls. A single layer "pure" amorphous a-C:H coating (without doping elements), having a Cr-based adhesion promoting interlayer was used for this investigation. A hybrid unbalanced magnetron sputter ion plating deposition system was used to deposit the a-C:H coating on steel balls and discs. Table 1 depicts important material properties.

Table 1. Important properties of the substrate and coating materials.

Element	Sample geometry	Hardness (GPa)	Young's modulus (GPa)	Average thickness (μm)	Roughness *R*a (μm)
Substrate : 440C stainless steel	Ball	8.3	200	-	0.03
	Disc	8.3	200	-	0.05
Coating: Cr-based interlayer a-C:H DLC coating	Ball	21.9	157	1.62	0.02
	Disc	21.9	157	1.62	0.06

Table 2. Properties of Canola oil.

Properties	Canola oil
Kinematic Viscosity at 40°C (mm^2/s)	35.476
Kinematic Viscosity at 100°C (mm^2/s)	8.1073
Viscosity Index	213.3
Density (Kg/m^3)	904.4
Oxidation Stability 110°C,h	0.06

Table 3: Fatty acid composition (%Wt.) of Canola oil.

Fatty Acid	Oleic 18:1	Linoleic 18:2	Palmitic 16:0	Stearic 18:0	Linolenic 18:3	Arachidic 20:0	Saturated	Monounsaturated	Polyunsaturated
Canola oil	62.58	30.28	4.55	1.85	9.75	1.46	14.6	23.7	42.5

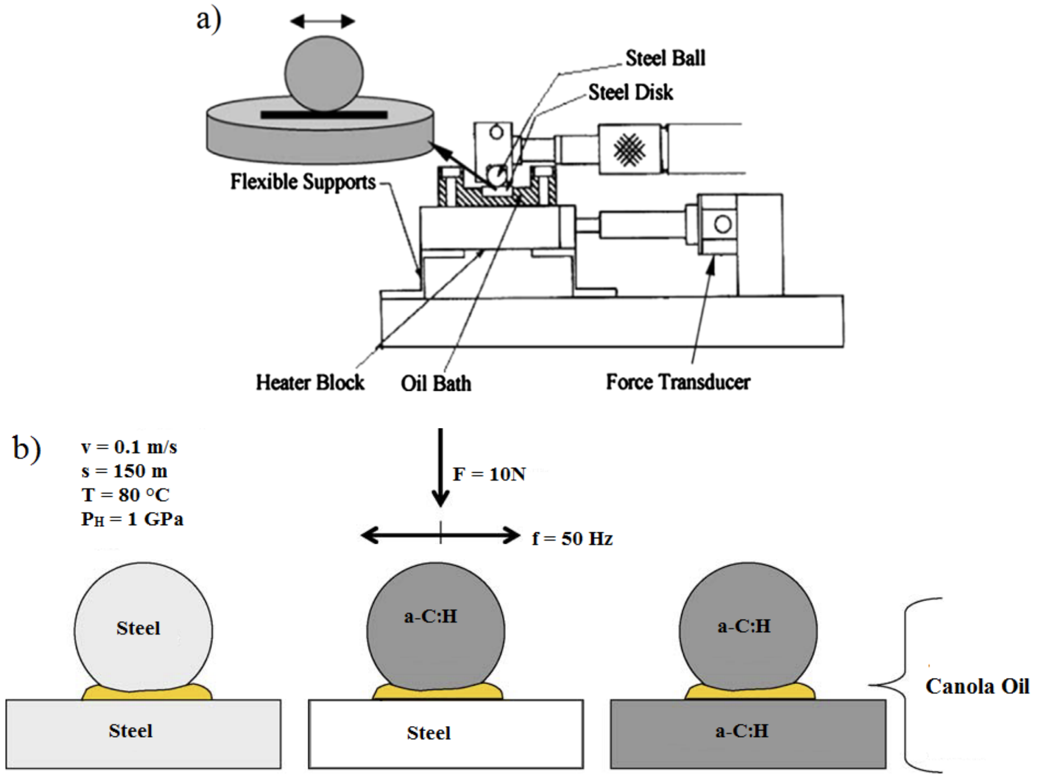


Fig. 1. HFRR test: a) schematic diagram of HFRR, b) materials and experimental condition.

In this experiment, Canola oil was used as lubricant. Some of the most important properties and the composition of fatty acids of Jatropha oil are shown in Table 2 and Table 3. The ball-on-flat reciprocating machine was used to perform the tribological tests. The flat sample was clamped in the base and the ball was clamped in the oscillating holder. Using stationary loading system, a 10 N load was applied, which produced a calculated 1 GPa initial Hertzian contact pressure. The stroke was 1 mm and the oscillating frequency 50 Hz, which provided mean contact velocity, 0.1 m/s. Before testing, the mating surfaces contacted each other; several drops of equal amount of oil were spread on the flat sample. After the start of the experiment, no extra oil was supplied to the contact. The bath temperature was pre-set to 80 °C in order to ensure high severity of the contact and the friction couple was tested for up to 72,000 cycles, corresponding to a total sliding distance of 150 m. Before testing, all the samples were ultrasonically cleaned in ethanol. Schematic diagram of HFRR and the major parameters, materials and conditions are presented in Fig. 1.

Throughout the testing, the coefficient of friction was simultaneously monitored as a function of cycle numbers. After the experiments, an optical microscope was used to measure the diameter of the wear scar on the ball. Then, the volume of the worn ball cap was calculated. A scanning electron microscope equipped with a Si-Li energy dispersive (EDS) detector was used to investigate worn surface of ball and disc. Investigated all balls and discs and consider maximum one for analysis. SEM and EDS measurements were taken on DLCs before and after testing and SEM micrographs were obtained at 15 kV accelerating voltage, 60 µA probe current and observed at x2000 magnification, in BSE mode. Also, the coating and wear areas were analyzed by RAMAN spectroscopy to investigate the change of deposited coating and wear of the coating. RAMAN spectroscopy LASER 514 nm wave length is used.

3. RESULTS AND DISCUSSION

In this investigation, "pure" non-doped DLC coating was used to appraise the tribological behavior of coating with Canola oil lubrication. Fig. 2 shows the friction curves of different material combinations, when lubricated with Canola oil. The friction coefficient is a prime factor, which indicates how much energy is lost to overcome the friction between the contacting surfaces. As can be seen in Fig. 2, a-C:H/a-C:H combination gave the lowest value of friction coefficient, around 0.07, with Canola oil, followed by steel/a-C:H, around 0.08, and steel/steel, around 0.14. From Fig. 2, steel/a-C:H material combination shows very uniform friction curves. The uncoated steel surfaces material combination showed higher friction value. The coefficient of friction of a-C:H coated material was approximately 42-50 % lower than that of the uncoated material. The reason behind the lower friction of a-C:H coated material with Canola oil lubrication is the large amount of polar components of oil that promotes the lubricity by forming a lubricating film with a-C:H coatings and the graphitization of a-C:H coating. In a-C:H/a-C:H contacts and steel/a-C:H contacts, almost same type of behavior has been found due to the absorbed water molecules and other oil impurities and others from the surrounding atmosphere [19-21] that adulterate the coating surface and endorse more interactions between the coatings and the oil. The anticipated wear reducing action of the Canola oil may be ascribed to the wear reduction in a-C:H coating and steel contact [22].

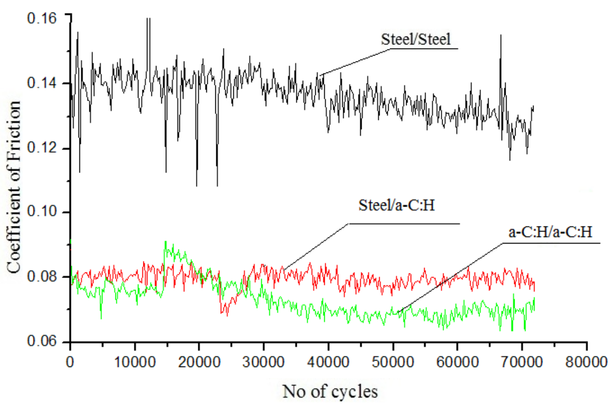


Fig. 2. Coefficient of friction of steel/steel, steel/a-C:H and a-C:H/a-C:H combinations with Canola oil lubrication.

The wear loss was determined by measuring the diameter of wear scar of the balls and subsequent calculation of the weight of the corresponding ball and disc. Fig. 3 shows the wear loss of several selected combinations. The results show remarkable discrepancies in the wear behavior for the experiments with Canola oil lubrication, when at least one surface was a-C:H DLC coated. For the steel/a-C:H combination, the lowest wear was found around 0.0025 mm^3, followed by a-C:H/a-C:H around 0.00275 mm^3 and the combination steel/steel around 0.0032 mm^3. For the a-C:H/a-C:H combination, the wear was approximately 9 % higher than that for the steel/a-C:H combination. The reason behind the higher wear loss of self-melted a-C:H surfaces is the a-C:H DLC coating film under strain and thermal effects produced by repeated friction cycles with lubricant, due to distorted film and graphitization of a-C:H coating in the wear track region [23]. In steel/a-C:H combination with Canola oil lubrication, the wear was reduced more than approximately 22 % as compared to that obtained for steel/steel contacts. The anticipated wear reducing action of the Canola oil may be ascribed to the wear reduction in a-C:H coating and steel contact. However, the almost same effect was also observed in the a-C:H/a-C:H contacts, which clearly indicates the lubrication effect of the Canola oil on the coating, due to above-discussed high availability of unsaturated and polar molecules in this oil.

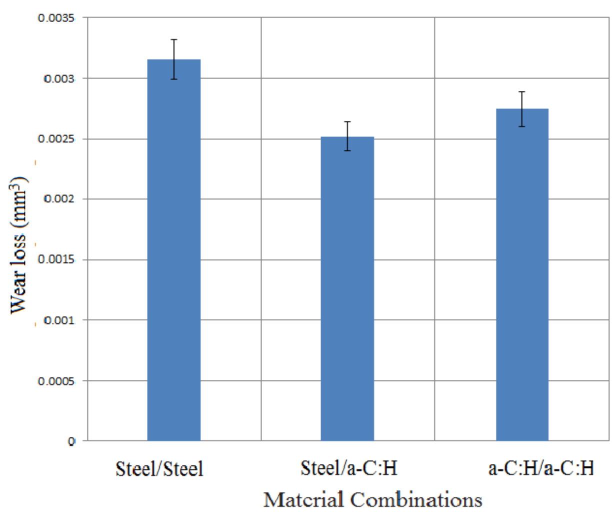


Fig. 3. Wear loss of selected ball and disc sets of steel/steel, steel/a-C:H and a-C:H/a-C:H material combinations, when lubricated with Canola oil. Error bars represent ± one standard deviation of the measurements.

The morphologies and chemical elements distribution of the worn ball surfaces were analyzed by SEM with EDS. The measurements were taken on a-C:H DLC coated surface before and after the tribological test. SEM micrographs were obtained at 60 μA probe current, 15 kV accelerating voltage, observed at x2000 magnification, in BSE mode.

Fig. 4 shows the SEM micrographs with wear scar diameter of the balls, when lubricated with Canola oil. From these images, it is possible to evaluate the anti-wear ability of a-C:H DLC coating and Canola oil. This experiment points out abrasive wear, adhesive wear, fatigue wear and corrosive wear. The appearance of the worn surfaces seems to present corrosive product of black color, mostly responsible because, at high temperature, the Canola oil is oxidized and produces corrosive acids, which enhance corrosive wear.

For the steel/steel combination, relatively high wear was observed with Canola oil lubrication (Fig. 4b). The steel/a-C:H material combination (Fig. 4c) shows lower wear and the SEM analyses confirmed this behavior, some signs of adhesion could be found on the contacts. The surfaces were very smooth and the reaction products could be confirmed with EDS analyses, as shown in Fig. 5c.

A distinctive layer was found, with amorphous like appearance, on the surface, as shown in Fig. 4c. The layer is a typical tribo-chemical layer and soft [24,25] and it can be the result of severe smearing and plastic deformation. Moreover, a-C:H coated materials combination with steel and itself (Fig. 4c&d) exhibit smooth worn surfaces, when they are lubricated with Canola oil found not considerable wear. It is well known that a-C:H DLC coating is a layer by layer structure and between each layer there is a week Van der Waals force, therefore these layers can slide easily among each other.

This phenomenon can be elucidated by attributing a transfer layer onto the counter surface formed by a-C:H DLC coating. The transfer layer contained finely distributed graphite nano particles. Also, Canola oil promotes the adsorption on metal surface due to chemistry nature of the oil and its polarity reduced wear, forming a thin layer for better metal-to-metal separation.

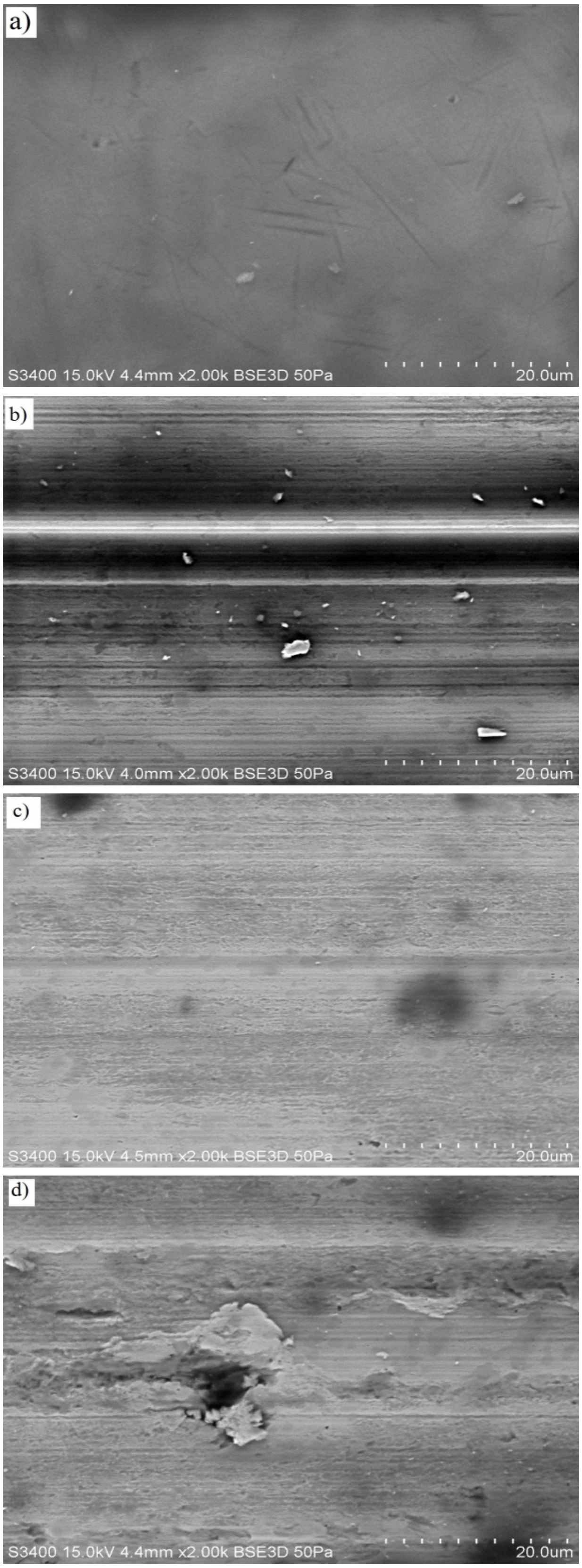
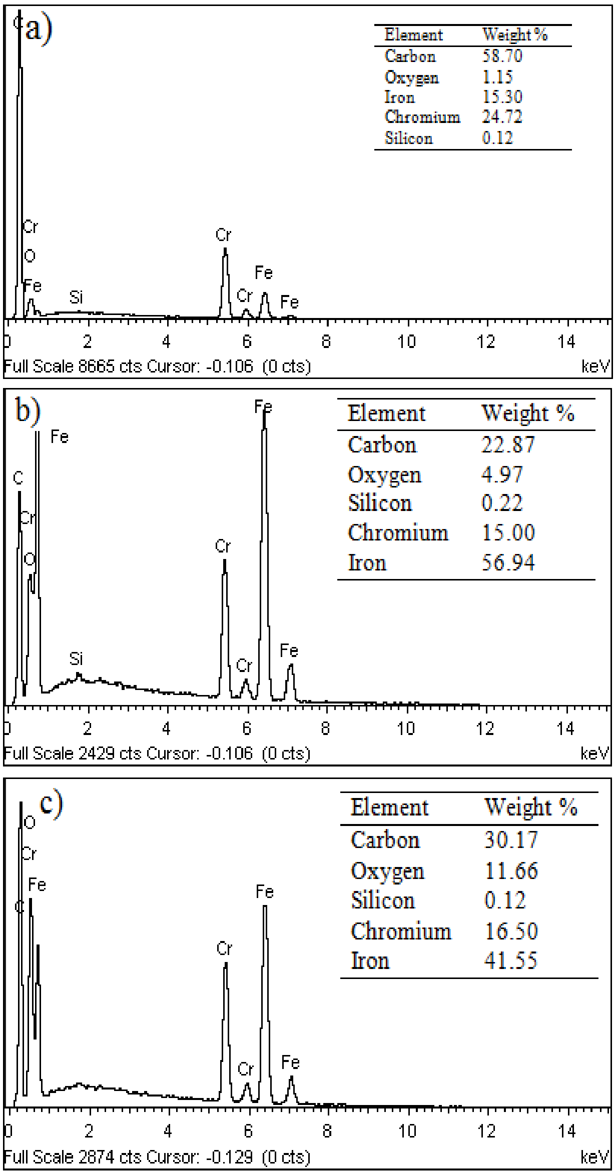


Fig. 4. SEM micrographs of the balls surfaces a) deposited surface of a-C:H DLC films; and worn surfaces when lubricated with Canola oil: (b) steel/steel (WSD = 416± 1.6 μm) (c) steel/a-C:H (WSD = 318± 1.3 μm) and (d) a-C:H/a-C:H combination (WSD = 355± 1.1 μm).

EDS analysis was conducted to evaluate the film formation on the worn surface, as shown in Fig. 5. These figures show the elementary analysis of the contact regions and the chemical elements present in areas indicated in Fig. 4. Based on Fig. 5, it was possible to evaluate the a-C:H DLC coating on wear reduction with Canola oil lubrication. The worn surface of steel/a-C:H combination (Fig. 4c & 5c) is smoother than a-C:H/a-C:H surface (Fig. 4d & 5d) than that of steel/steel surface (Fig. 4b & 5b). The a-C:H DLC film improves the film formation with Canola oil. Therefore, for at least one a-C:H surface, the obtained results are quite explicit and expected as well. As mentioned above, “pure” non-doped DLC (a-C:H) coated materials always caused lower friction due to the lower contribution of adhesion and lower overall friction due to their well-known anti-stick /low-adhesion properties.



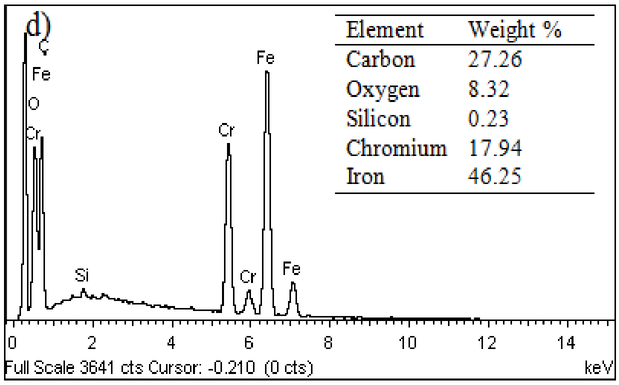


Fig. 5. EDS analysis of the balls surfaces a) as deposited a-C:H DLC films; and worn surfaces when lubricated with Canola oil: (b) steel/steel (c) steel/a-C:H and (d) a-C:H/a-C:H combination.

The steel/steel contact has higher adhesion affinity than that of steel/a-C:H contact [26]. In fact, a-C:H DLC film has very good anti-sticking behavior [27-30]. We can clearly see that from the tribological test: the friction in steel/a-C:H contacts is lower than that for the steel/steel with Canola oil lubrication, which absolutely supports the significant adhesive wear reduction. Also, steel/a-C:H contacts confirmed the significant improved abrasive wear resistance compared to that of the steel/steel. Furthermore, the number of abrasive scratch grooves and the reduced plastic deformation at the a-C:H DLC surfaces also lead to reduce fatigue effects and contribute to reduce stress concentrations during a longer period of operation. Another very important and interesting phenomenon was observed during the tribological tests. Namely, a coherent and well adhered thick boundary film was observed in SEM images (see Fig. 4). The existence of an amorphous transfer film from the a-C:H DLC coated surface to the steel surface and its serious significance in improving the friction behavior was reported earlier and this transfer film concept has proven to be very efficient under steel/a-C:H sliding conditions [28,31]. In such a situation, a carbon transfer film layer is sliding against the a-C:H DLC, providing very low friction [32,33]. Our experiment outcomes suggest very similar behavior and the dramatic reduction of the friction in the steel/a-C:H contacts, the key reason is the amorphous nature of this coherent film that appears.

Moreover, recent detailed studies of steel surfaces and a-C:H DLC sliding in lubricated conditions using various surface sensitive techniques also stressed the importance of tribofilm formation [34,35]; however, the films forming at a-C:H DLC and the steel surfaces were not the same [34-37]. Namely, the hydrogenated DLC coating at the interface reacts with the oil and forms OH and CH groups [34], which suggest that, at the DLC surface, it prevents from adhesive interactions by the carboxyl and hydroxyl groups [35]. While at steel counterface only hydroxyl groups were found [36], see Fig. 5. From this, it is obvious that the in-situ forming interface layers on both contacting materials are very relevant for the friction behavior. To confirm the existence of such a tribofilm found in tribological tests, EDS analysis was done (Fig. 5). Thus, it is very clear that by employing the a-C:H DLC coating against steel in Canola oil lubricated condition the friction is significantly reduced the friction behavior and improved the overall tribological behavior, which opens up new opportunities for further developments of automotive components, which suffer a lot from wear and friction when used with conventional steel materials.

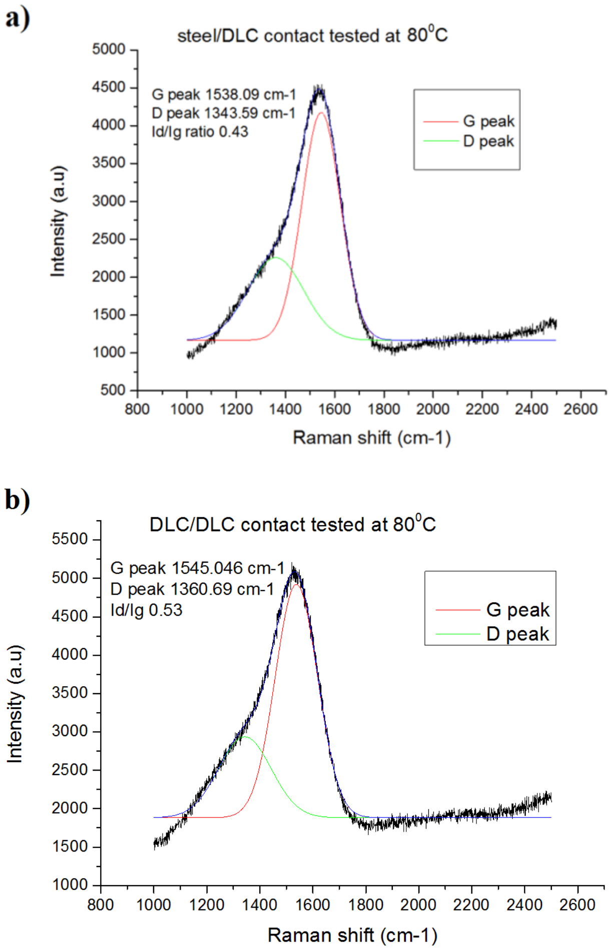


Fig. 6. RAMAN analysis of the a-C:H DLC coating wear track.

Raman analysis for different combinations of materials is shown in Fig. 6. It has been found that steel/DLC contact shows lower graphitization, which is confirmed by Id/Ig ratio of the wear track as compared to the results obtained for DLC/DLC contact wear track. For the steel/DLC contact, Id/Ig ratio is 0.43 and for DLC/DLC contact, it is 0.53, which clearly confirms the higher degree of graphitization in the DLC/DLC contact and facilitates the slip in the contact area, which further results in a lower coefficient of friction of DLC/DLC contact [38]. It has been shown that (Fig. 6), comparing both contacts, G peak and D peak positions shifted to higher wave numbers for the DLC/DLC contact, which is another evidence of graphitization. Peak height is also shifted to higher intensity as compared to the steel/DLC contact. All these changes that has been proved by Raman peak deconvolution into G peak and D peak, clearly confirm the higher degree of graphitization for the DLC/DLC contact, for the present experimental conditions [39].

4. CONCLUSION

Based on the experimental study, the following conclusions can be drawn:

1. The a-C:H DLC coating with Canola oil lubrication significantly reduced the coefficient of friction and the wear loss.
2. The tribological properties of the a-C:H coating are significantly improved due to the availability of large amount of polar components in the Canola oil.
3. The coefficient of friction of a-C:H coated materials was about 42-50% lower with Canola oil lubrication as compared to the uncoated materials combination.
4. The a-C:H/a-C:H combinations showed the lowest coefficient of friction around 0.07 as compared to other combinations.
5. The steel/steel and steel/a-C:H combinations have shown a very uniform curve for the coefficient of friction.
6. Under boundary lubrication conditions, the wear of steel/a-C:H combination was the lowest in this investigation, when lubricated with Canola oil.
7. Wear loss of the steel/a-C:H combination was the lowest, around 0.00250 mm^3,

followed by the couple a-C:H/a-C:H, around 0.00275 mm^3 and the couple steel/steel, around 0.00325 mm^3.

8. The a-C:H/a-C:H combination showed approximately 9% higher wear loss than that obtained for steel/a-C:H combination.
9. The combination a-C: H coated materials with steel and itself exhibit smooth worm surfaces when lubricated with Canola oil and found not considerable wear.

Thus, usage of a-C: H DLC coating when lubricated with Canola oil may have a positive impact on engine life in the long run. This study may support the establishment and encourage research of a-C: H DLC coating, combined with renewable natural sources as alternative lubricants for automotive components.

Acknowledgments

The authors would like to address an acknowledgement to the Department of Mechanical Engineering, Dhaka university of Engineering and Technology, Gazipur, Bangladesh and University Research Grant.

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