Optimizing the tribological performance of DLC-coated NBR rubber: The role of hydrogen in films

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Received: 25 April 2020 / Revised: 31 December 2020 / Accepted: 26 January 2021

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Abstract: Diamond-like carbon (DLC) films directly deposited on rubber substrate is undoubtedly one optimal option to improve the tribological properties due to its ultralow friction, high-hardness as well as good chemical compatibility with rubber. Investigating the relationship between film structure and tribological performance is vital for protecting rubber. In this study it was demonstrated that the etching effect induced by hydrogen incorporation played positive roles in reducing surface roughness of DLC films. In addition, the water contact angle (CA) of DLC-coated nitrile butadiene rubber (NBR) was sensitive to the surface energy and sp² carbon clustering of DLC films. Most importantly, the optimum tribological performance was obtained at the 29 at% H-containing DLC film coated on NBR, which mainly depended on the following key factors: (1) the DLC film with appropriate roughness matched the counterpart surface; (2) the contact area and surface energy controlled interface adhesive force; (3) the microstructure of DLC films impacted load-bearing capacity; and (4) the generation of graphitic phase acted as a solid lubricant. This understanding may draw inspiration for the fabrication of DLC films on rubber to achieve low friction coefficient.

Keywords: rubber; DLC films; hydrogen; contact angle; tribological performance

1 Introduction

Efficiently reducing the friction and wear of dynamic rubber seals can greatly prevent leakage, maintain gas pressure, and exclude dirt, thereby benefiting to energy conservation and environmental protection [1–3]. Considerable methods have been devoted to optimize the friction performance of dynamic rubber seals. Among them, surface modification is a widely used method to impart desirable long-term effects for safeguard of rubber seals [4–7]. The alteration of rubber surface properties such as hydrophobicity and roughness will inevitably lead to the change of friction behavior, which provides an opportunity

to govern friction behavior with regard to dynamic rubber seals [8]. Therefore, a variety of techniques, including chemical and physical techniques, have been developed to modify the rubber surface.

Chemical techniques, such as surface halogenation, sulfonation, and oxidation, are often applied to change the compositions on rubber surface [9]. Unfortunately, the chemical treatments often have many disadvantages, such as environmental pollution and seal swelling under the condition of oil medium [10]. In comparison, in terms of environmental protection and the potential industrial applications, it is of great significance that physical techniques are extensively adapted to realize the low friction state for rubber [11]. One

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of the effective physical modifications is to deposit diamond-like carbon (DLC) films on rubber as a protective layer [12, 13], where various deposition technologies including plasma enhanced chemical-vapor deposition (PECVD) [14], femtosecond pulsed laser ablation [15], magnetron sputtering (MS) [16] and so on are applied. Unlike the carbide and nitride coating that possessed high friction under unlubricated conditions, DLC films show low friction when sliding against most counterpart surfaces. Moreover, the mechanical properties of DLC films could be adjusted by the presence of dopants, such as W, Cr, Si, and F, or by changing the kinetic energy of incident particles [17–19]. Crucially, since DLC films behave superior affinity to rubber, it ensures a potentially good adhesion [20].

The low friction of DLC films has been generally explained by two mechanisms. The first one is shear-induced graphitization where sp^3 -C is transformed to sp^2 -C [21]. The second one is that the surface dangling bonds are passivated by H molecule at the friction interface [22]. Obviously, the above friction mechanisms are obtained by depositing DLC films on hard substrate, while the governing factor for the lubrication performance and film structure evolution of the DLC-coated rubber remains unknown. In addition, the influence of hydrogen contents in films on the hydrophobicity and friction performance of DLC-coated rubber is yet to be clarified. Therefore, this work explores the governing factor to friction properties of DLC-coated rubber by introducing the hydrogen plasma to manipulate film structures and morphologies, aiming to produce high-performance dynamic rubber seals.

2 Experimental details

2.1 Film preparation

DLC films were fabricated on NBR in a plasma discharging system (Fig. 1(a)). First, the NBR pieces were bombarded by argon plasma for 30 minutes to eliminate oil contamination (residual soap and wax) [7]. Next, in the mixed working atmosphere of methane (10 sccm, 99.99%) and argon (100 sccm, 99.99%), a buffer layer of thin carbon film was prepared at negative voltage of 800 V for 10 min to

guarantee the fine adhesion of DLC films with different hydrogen contents on NBR. Finally, during DLC films deposition process, methane with a constant flow rate of 20 sccm and hydrogen with the different flow rates of 10, 20, 30, and 40 sccm were used as reaction gas sources. The negative voltage of 800 V, frequency of 60 kHz, and duty cycle of 60% were applied. The thickness of DLC films with different hydrogen contents was about 700 ± 60 nm (Fig. S1 in the Electronic Supplementary Material (ESM)). The deposition chamber temperature, which was monitored by a thermometer putted above sample tray, was kept at 75 ± 5 °C by water cooling system to lower the temperature effect, because the surface morphology of DLC-coated rubber depended on the variation of temperature [23]. The schematic process of temperature change in the process of DLC films preparation is displayed in Fig. 1(b).

2.2 Microstructure characterization

The Raman spectroscopy was acquired by Czerny-Turner Labram HR800 spectrometer using the argon ion laser with a wavelength of 532 nm. The roughness of DLC films was characterized by atomic force microscopy (AFM, Bruker Co.). To remove the influence of substrate deformation, the hardness was measured on DLC films coated on Si wafer where the same deposition conditions were used as those of DLC films coated on NBR. The test was conducted on nanoindenter (Hysitron Ti-950), and the indentation depth was 80 nm. Although the measured hardness value is higher than that of DLC-coated NBR, it is expected that their hardness would show the same trend [24]. The morphology of wear tracks was examined using scanning electron microscope (SEM, JSM-6701F). X-ray photoelectron spectroscopy (XPS, PHI-570) was employed to investigate the chemical composition of as-deposited films and wear tracks surfaces.

2.3 Static contact angle (CA) measurements

DSA100 CA measurement instrument (KRÜSS, Germany) was used to measure the static CA, where a droplet of 1 μ L (diiodomethane and water) was adopted by the sessile drop method. The static CA value at steady state after 15 seconds was collected

for each of the measurements. Owens–Wendt–Rabel–Kaelble (OWRK) method was applied to estimate the surface energy of DLC-coated NBR [25]. The formula is as follows:

$$\gamma_L(1 + \cos\theta) = 2(\gamma_S^d\gamma_L^d)^{1/2} + 2(\gamma_S^p\gamma_L^p)^{1/2}$$

where θ represents averaged CA, γ^d and γ^p stand for the dispersive and polar components of surface energy, and subscripts S and L refer to solids and liquids, respectively.

2.4 Tribological Tests

A ball-on-disc tribometer was utilized to characterize the tribological performance under a constant humidity (25%±3%) with room temperature (25 °C). The commercial ø6 mm GCr15 steel balls were selected as the counterpart materials. The tests were performed under the normal load of 3 N, rotational speed of 83.73 mm/s (rotation radius of 4 mm), and duration time of 60 minutes. All tribo-tests were implemented at three times to guarantee the reproducibility.

3 Results and discussion

Raman spectra recorded from DLC films can identify

sp²/sp³ ratio, vibration mode, and bond length disorder (Figs. 1(c) and 1(d)). Apparent peaks are ascribed to the prominent G peak and a smaller shoulder D Peak, which represents the stretching vibration of sp² carbon atoms and the breathing vibration of sp² bonds in the rings only, respectively [26]. Normally, the sp²/sp³ ratio in hydrogenated amorphous DLC films can be derived from I_D/I_G ratio and the G peak position [27]. However, the deconvolution of CH-sp¹, CH₂-sp², and CH₃-sp³ is challenging as the C–H stretching vibration bands are broad (about 2,400–3,400 cm⁻¹). So, Raman analysis is only performed to compare the number of C–H bonds by peak stretching mode intensity [28]. Obviously, an increase in the intensity of C–H stretching vibration corresponds to that the hydrogen content in films increases monotonously with the rise of the proportion of H₂ discharge plasma (Fig. 1(c)).

To further investigate the bonded hydrogen content, the ratio of the spectral background slope (m) and the G peak intensity (I_g) is employed to calculate the atomic percentage, as hydrogen content in DLC films prepared by pure and increasingly hydrogenated CH₄ gas discharge plasma can affect the photoluminescence background [29].

Fig. 1 (a) Illustration of plasma discharging system (PECVD). (b) Graphical description of the deposition process of DLC-coated NBR. (c) Raman spectra of DLC-coated NBR samples from 2,200–3,600 cm⁻¹ and (d) the deconvolution in 700–2,100 cm⁻¹ (D and G peaks).

$$H \text{ (at.\%)} = 21.7 + 16.6 \log \left\{ \frac{m}{I_g} [\mu\text{m}] \right\}$$

The results clearly reveal that the increasingly hydrogenated CH₄ gas discharge plasma performs in favor of the rise of the hydrogen atomic percentage in DLC films (Table 1). It could also be found that the rise rate of hydrogen content in films gradually slows down, which may be attributed that the interfacial, unstable carbon atoms affiliated to unrelaxed domains can be etched away by hydrogen ion bombardment [30]. Additionally, the increasingly hydrogenated CH₄ gas discharge plasma possesses the lower electron density, thus leading to a drop of decomposition efficiency of methane [31]. This process may promote a decrease in probability of the preferentially nucleated groups (C–H bonds) in DLC films. Note that, the real potential applied on rubber surface may be lower than that of the applied negative electrical bias, as the NBR rubber is a good dielectric. Therefore, the part of hydrogen may exist in some other modes, which might not to bond with carbon and solely exist as molecules and isolated atoms [32].

The deconvolution of Raman spectra in the wavenumber of 700–2,100 cm^{−1} indicates the G peak position gradually moves toward the higher wavenumber with increase of H₂ flow rate (Fig. 1(d)). Moreover, combined the sharp increase of I_D/I_G (Table 1), it can be deduced that the rearrangement of the sp² carbon clusters is occurred with increase of H₂ flow rate. The reason may be attributed that the unstable phase is etched by the H plasma, and H emission decreases the internal stress and the degree of distortion, resulting in DLC films achieving a steady state through local rearrangement [33]. So,

Table 1 Overview of I_D/I_G ratio, G peak position, mechanical properties of DLC films.

Ratio of CH ₄ /H ₂	Hydrogen (at%)	I_D/I_G	G peak (cm ^{−1})	H (GPa)	E (GPa)
1/0	24	0.48	1527	24.8±0.5	145.5±5
2/1	26	0.49	1528	23.2±0.8	140.3±2
1/1	29	0.51	1531	21.8±0.6	134.3±2
2/3	30	0.53	1533	20.9±0.6	128.6±5
1/2	31	0.53	1534	19.8±0.9	129.6±4

hydrogen atoms can promote the topological order of the graphite phase and the increase of the aromatic hydrocarbon bond. Besides, the amorphous property and poor thermal conductor of NBR rubber may accumulate sufficient plasma activation energy and lead to random nuclei of graphite phase [34]. The load–displacement curves further demonstrate that DLC films prepared by the increasingly hydrogenated CH₄ gas discharge plasma own relatively inferior mechanical properties (Fig. S2 in the ESM), where the normal force gradually decreases with increase of hydrogen content under the same indentation depth. Using Oliver and Pharr’s method, the hardness (H) and elastic modulus (E) are calculated and summarized in Table 1. Generally, the hardness of DLC films mainly depends on the existence of sp³ bonds (diamond-like carbon). On the contrary, it is believed that sp² bonds (graphitic-like carbon) will soften the film [26, 27]. Therefore, the high hydrogen content impairs the bearing capacity for DLC films, which can be ascribed to the enhancement of graphite phase via H plasma etching [33].

Figure 2 reveals the three-dimensional morphology of uncoated and DLC-coated NBR measured by atomic force microscopy. There is a significant difference between virgin and DLC-coated NBR that all deposited DLC films exhibit a “cauliflower-like” morphology and have higher surface roughness than that of virgin NBR substrate. It is well known that the depression on NBR surface is a predominant position where activated carbon particles gather [35]. In this work, the virgin NBR rubber is smooth and the exposed depressions are evenly distributed and discrete. In the initial stage of film growth, the nucleation sites mainly concentrated around the depressions, and the growth rate of DLC films at the depressions is higher than other position. Eventually, the surface morphology of DLC films in the form of “hills” tends to have higher roughness compared to virgin NBR. Noteworthy, Liu et al. [35, 36] reported that the fabrication of the DLC film is beneficial to lower the surface roughness of NBR. Our results are contrary to previous study, which may be related to the thickness of films, the distribution and size of the depressions on rubber, and the effect of Ar plasma pretreatment. Apparently, the larger

Fig. 2 AFM images of (a) uncoated NBR and DLC films deposited on NBR with different ratios of CH_4 and H_2 of (b) 1/0, (c) 2/1, (d) 1/1, (e) 2/3, and (f) 1/2.

thickness of DLC films on the flexible substrate results in the greater strain energy in the film. We believe that, to relax the strain energy, the growth mode of DLC films would be dominated by the island growth mode when the thickness of film reaches a critical value, thus conducting the increase of surface roughness of DLC-coated NBR.

With a clearer understanding of the effect of the H plasma on DLC films roughness, it is noting that the increasingly H_2 gas discharge plasma can promote the reduction of film's roughness (Figs. 2(b)–2(f)). The phenomenon is related to plasma species and film structural changes (the emission of hydrogen and graphitization) [37]. Hydrogen is used as a reactive gas, where activated and ionized hydrogen molecules can etch clusters of DLC films [30], thereby leading to a reduction in the size of the cluster of DLC-coated NBR. Furthermore, the stress alleviation and smoothness of DLC films can also derive from carbon atoms rearrangement and sp^2 aggregation in the priority orientation [38, 39]. Therefore, it can be seen that the increase of hydrogen plasma is conducive to reduce the roughness of DLC-coated NBR.

Water CA measurement is an effective means to testify the surface wettability of DLC-coated NBR. The angle θ formed by liquid–gas interface of the equilibrium state represents contact angle when a small water liquid drops to substrate surface [25]. The result shows that depositing DLC films is beneficial

to improve the hydrophobicity of NBR (Fig. 3(a)), which may be due to surface roughness plays a major role to enhance the hydrophobicity [40]. Next, by comparing the hydrophobicity of DLC-coated NBR, one can find that the water CA continuously increases for DLC films prepared with the increasingly hydrogenated CH_4 gas discharge plasma. Considering the AFM micrographics of all samples, this phenomenon is contrary to the theory that roughness affects hydrophobicity. Apart from roughness, the surface energy is the definitely major parameter to adjust the surface wettability. It is generally believed that higher surface energy is beneficial to lower CA. Surface energy is usually obtained by using the contact angle measure of two solutions with big polarity and the OWRK method [25]. Apparently, as summarized in Fig. 3(b), it can be found that DLC film is conducive to reduce surface energy of NBR, and the DLC film prepared with the increasingly hydrogenated CH_4 gas discharge plasma possesses lower surface energy. As reported by Wen's group, lower surface energy is conducive to the aggregation of carbon atoms and the formation of films, thereby promoting the drop of film roughness [35]. Furthermore, previous studies indicated that the sp^3 rich phase surfaces of DLC films exhibited lower CA than sp^2 rich phase surfaces [41]. It can be concluded that the enhancement of CA of DLC films prepared with the increasingly hydrogenated CH_4 gas discharge

Fig. 3 (a) Steady-state CA values and images of a water drop. (b) Total and component surface energies calculated by the OWRK method on uncoated and DLC-coated NBR with different ratios of CH₄ to H₂.

plasma is mainly related to the reduction of surface energy and the increase of sp² carbon clustering. Thus, we deduce that hydrophobicity of DLC-coated NBR is more sensitive to the surface chemistry than the surface roughness.

Friction behaviors of uncoated NBR and DLC-coated NBR sliding against steel balls tests were investigated, as shown in Fig. 4(a). The friction coefficient of NBR rubber increases gradually to high values before 5,000 cycles and then decreases to 0.82 and remains thereafter, indicating that the friction process enters a steady period. The phenomenon is supported by the theory that the overall contribution to friction force of rubber sliding against hard counterpart is the adhesive interaction and the hysteresis effect [42]. The partial destruction of NBR rubber surface is initially appeared, and a stable oxide layer is finally formed as the lap increase. Correspondingly, the adhesive force first increases

and then decreases. In addition, rubber molecules become easier to move due to friction heat generation causing thermal expansion of rubber, resulting in the reduction of the hysteresis component [5]. Therefore, the steady friction period and anti-tear properties of NBR rubber are achieved by reducing adhesive and hysteresis component. Note that, once DLC film is fabricated on NBR, it immediately weakens the interface interaction between NBR and counterpart, leading to a dramatic drop in friction force. A significantly low friction coefficient ($\mu < 0.2$) and the most effective one showing 74% friction reduction can be monitored for the 29 at% H-containing DLC film (Fig. 4(b)). It is also found that the DLC film is conducive to minimize fluctuations of friction curves, obtaining the excellent stability of lubricating state. The friction performance of DLC films prepared with the increasingly hydrogenated CH₄ gas discharge plasma is discussed in detail later.

Fig. 4 (a) Friction curve of uncoated NBR and DLC-coated NBR with different ratios of CH₄ to H₂, insert shows initial friction value. (b) Average friction coefficient of each group after three repetitions.

Microscopic examination of morphologies on wear surfaces is revealed in Fig. 5. After the friction test, the outer fringe of wear track of virgin NBR has a trend of “liquid-like” third body adhering, and the contact area of GCr15 steel ball is completely covered by friction generated materials (Fig. 5(a₁)). Evidently, the interface adhesion force between metal counterpart and NBR can be weakened by depositing DLC films, thereby providing low wear and friction coefficient. It can be seen that the wear on the 24 at% H-containing DLC film occurs at the “hill” of the sample (Fig. 5(b)), and the wear debris is visible around the counterpart surface and the transferred material is relatively little. Conceivably, the unstable sliding interface is responsible for such high friction coefficient. With the increase of hydrogen content in DLC films, the size of wear scar is larger, the wear track is relatively clean, and the fragment generation is no detectable. Closer observations illustrate that sliding-induced surface polishing occurs on the wear scars on GCr15 steel ball (Fig. 5(c₁)), which is supported by the exposure of bright zones. However, the counterpart used during the tribo-tests of the 31 at% H-containing DLC film shows much adhesive wear, as evident from the plentiful tribo-debris produced in the wear tracks and around the wear scars (Figs. 5(d) and 5(d₁)). The 31 at% H-containing DLC films’ inferior friction performance may arise from lower hardness. These results provide convincing observations of poor lubrication in terms of abrasive wear in film containing low hydrogen content and adhesive wear in film containing high hydrogen content. Furthermore, the structural transformation between contacting

surfaces needs to be further discussed.

The tribo-chemical reaction of the sliding interface is also believed to render the significantly improved friction performance for the 29 at% H-containing DLC film (Fig. 4(b)). Hence, XPS is utilized to distinguish the variation of bonding of 29 at% H-containing DLC film and its wear track (Fig. 6). The C 1s core position (284.4 eV) of wear track is closer to that (284.3 eV) of graphite in comparison with that (284.6 eV) of DLC films. The deconvolution of the XPS spectrum from wear track reveals an increased ratio of sp² carbon bonds (peak position at 284.3 eV) and a decreased ratio of sp³ carbon bonds (peak position at 285.1 eV) compared to the unworn surface of the 29 at% H-containing DLC film (Fig. 6). Therefore, it is speculated that a newborn friction interface with low shear force is formed by the graphitization process. It is considered that the release of hydrogen from DLC may result in a transformation of sp³ carbon to sp² carbon during friction process [28]. In addition, in view of the large contact area potentially facilitating adhesive interaction (Fig. 5(c₁)), the sp³ bonds may be condensed and convert into thermodynamically stable sp² bonds [43]. The pre-discussions certified the graphitization process was one of the keys to achieve a low shear sliding interface between the DLC-coated NBR and counterpart.

Based on the systematic investigation of the surface morphology, surface energy, and tribological behaviors of DLC-coated NBR, a feasible friction mechanism of DLC-coated NBR is displayed as shown in schematic process (Fig. 7). For the low H-containing DLC film coated on rubber (Fig. 7(I)), the friction

Fig. 5 SEM characterization of wear tracks of (a) NBR and DLC films deposited on NBR with different ratio of CH₄ and H₂ of (b) 1/0, (c) 1/1, (d) 1/2, and (a₁–d₁) the corresponding counterpart surfaces.

Fig. 6 The C 1s XPS spectra of the 29 at% H-containing DLC film worn: (a) before and (b) after.

Fig. 7 Schematic diagram of friction evolution between counterpart and DLC films prepared with different hydrogen contents on rubber: (I) the low H-containing DLC film, (II) the middle H-containing DLC film, and (III) the high H-containing DLC film.

coefficient has strong correlations with surface roughness, as the film has a tendency of being peeled off from the substrate during sliding process (Fig. 5(b)). The film with high roughness tends to form plough effect with counterpart, which causes the film failure and forms the abrasive particle that results in high friction coefficient. Another reason for the poor friction behavior may be attributed to the surface energy (Fig. 3(b)), as higher surface energy could result in a higher adhesion force between rough peak of DLC-coated NBR and steel ball. It is worth mentioning that the low H-containing DLC film coated on rubber exhibits the relatively high initial friction coefficient (Fig. 4(a) inset). This is the consequence of small contact areas and high roughness, which cause the front of the ball to bear

higher pressure and the back of the ball to receive lower pushing force (Fig. 7).

In terms of the high H-containing DLC film coated on rubber (Fig. 7(III)), the low hardness of films may have direct relation with tribological behaviors. It was reported that amorphous carbon film with high hardness on rubber would have better wear resistance [36]. The increasingly hydrogenated CH_4 gas discharge plasma promotes the formation of the graphite phase (Table 1), thereby reducing the hardness of the film and impairing the load capacity of the hydrocarbon network. It should also be recognized that the amorphous nature of substrate can enhance the arbitrary and excessive nucleation of graphite phase (Fig. 7(III)), thereby producing small grain size and impairing the mechanical properties of the

film [34]. In addition, the previous results demonstrate that hydrogen atoms passivate the dangling bonds generated on the friction interfaces and prevent the adhesive component [22]. However, the surface roughness of DLC-coated NBR plays a more important role, because the research indicates that the wear scar showed much adhesive wear (Fig. 5(d₁)). The large contact area between the relatively smooth DLC-coated NBR and counterpart can generate more adhesion sites, thereby increasing the adhesive component. To all appearance, the authors believe that the superior friction performance depends on the generated graphite-like carbon in wear track, the relatively low surface energy, and the film with appropriate roughness to match the counterpart (Fig. 7(II)). Therefore, the application of DLC films can significantly decrease the adhesive component, and the decrease of the hysteresis contribution is of secondary importance.

4 Conclusions

To summarize, introducing hydrogen plasma into deposition systems is emphasized for its vital role to adjust the microstructure, roughness, and surface energy of DLC films, which can strongly affect the tribological properties of DLC-coated NBR. It is worth noting that the rearrangement of the sp² carbon clusters is occurred with increase of H₂ flow rate, thereby reducing the hardness of DLC films and impairing the load capacity of the hydrocarbon network. Meanwhile, hydrogen plasma can enhance the etching effect and then lead to a reduction in the size of the cluster, which is conducive to reduce the roughness and the surface energy of DLC-coated NBR. Therefore, the low H-containing DLC-coated NBR has a tendency to peel off from substrate due to the high roughness and surface energy. Relatively, the high H-containing DLC-coated NBR possesses the highly sp² bonded, which leads to the decline of bearing capacity thereby reducing wear resistance. In addition, the larger contact area between the relatively smooth DLC-coated NBR and counterpart can generate more adhesion sites, thereby increasing the adhesive component. The suitable roughness and low surface energy of DLC films benefit to reduce

friction force, and a high sp³-bonded microstructure is desired for load capacity and the generation of graphite layer serves as lubricating film, which ultimately endow excellent friction performance ($\mu \sim 0.2$) for DLC-coated NBR. The comprehensive analysis of friction performance for DLC-coated NBR seals will provide a solid foundation for engineering applications.

Acknowledgements

This work is supported by the National Natural Science Foundation of China (Nos. U1737213 and 52005485), and Youth Innovation Promotion Association CAS (No. 2017459).

Electronic Supplementary Material: Supplementary material is available in the online version of this article at <https://doi.org/10.1007/s40544-021-0498-0>.

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