Adhesion and friction performance of DLC/rubber: The influence of plasma pretreatment

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Abstract: Diamond-like carbon (DLC) films are deposited on rubber surfaces to protect the rubber components, and surface pretreatment of the rubber substrates prior to the film deposition can improve the adhesion between the DLC films and the rubber. Thus, the principal purpose of this work concentrates on determining the effects of argon (Ar), oxygen (O₂), nitrogen (N₂), and hydrogen (H₂) plasma pretreatments on the adhesion and friction performance of the DLC films deposited on rubber (DLC/rubber). The results indicated that the Ar plasma pretreatment promoted the formation of a compact layer on the rubber surface. By contrast, massive fillers were exposed on the rubber surface after oxygen or nitrogen plasma pretreatments. Moreover, the typical micrometer-scale patches divided by random cracks were observed on the surface of DLC/rubber, except for the sample pretreated with oxygen plasma. The adhesion of DLC/rubber was found to strengthen with the removal of weak boundary layers and the generation of free radicals on the rubber surface after plasma pretreatment. The tribo-tests revealed that DLC/rubber with O₂, N₂, and H₂ plasma pretreatments cannot achieve optimal friction performance. Significantly, DLC/rubber with Ar plasma pretreatment exhibited a low and stable friction coefficient of 0.19 and superior wear resistance, which was correlated to the high adhesion, good load-bearing of the rubber surface, and the approximate sine function of the surface profile of the DLC film.

Keywords: diamond-like carbon (DLC) films; rubber; plasma pretreatment; adhesion; friction

1 Introduction

Friction and wear of rubber against rigid surfaces are important topics in the automotive (sealing, bushing), construction (roofing), and electronic (insulators) industries. Optimizing the friction performance of rubber components has been shown to contribute to minimized energy loss, increased overall efficiency of machines, and the

prevention of sealing fluid leakage [1, 2]. Particularly, many rubber components operate in unlubricated or lubricant-lacking environments. For example, the inlet gap of the contact zone cannot be completely filled with the lubricating medium at the startup of the reciprocating seal [3, 4]. Additionally, deteriorated metal counterpart surfaces and intruding external particles can promote surface crack propagation, and scratching

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and plowing of rubber surfaces [5, 6]. Therefore, investigations aimed at preventing rubber components from undergoing serious friction and wear are considered top priority projects.

Diamond-like carbon (DLC) films have garnered considerable interest as materials for lubrication and protection, due to the combination of relatively high hardness, ultralow friction, and excellent wear resistance [7–9]. Beyond that, DLC films not only possess promising chemical compatibility with the rubber (to prevent the degradation of rubber components) but the deposition temperature can be adjusted to be lower than the upper temperature limit of the rubber (by the choice of the deposition method and controlling process variables) [10–13]. Therefore, DLC films prepared on the rubber surface is undoubtedly a viable option. However, when a rigid protective film is deposited on flexible rubber substrates, interfacial delamination under load conditions is inevitable. To overcome this limitation, plasma modification of the rubber surface has been developed to improve the adhesion between the DLC films and rubber.

The improvement in adhesion between the DLC films and rubber by plasma pretreatment can be attributed to several major factors, including the removal of low molecular weight substances to obtain cleaned surfaces, the synergistic effects of chain scission and crosslinking, the generation of free active species on the upper surface, and the modification of the chemical structure and morphology of the rubber surface [14]. The adhesion of DLC/rubber was shown to increase by using Ar or Ar–H₂ plasma [15]. Moreover, a relationship between the film patch size and the adhesion strength has been established [16–19]. Furthermore, a multitude of research on O₂ plasma pretreatment for improving the strength of adhesion has been carried out. On the one hand, O₂ plasma can react with the rubber surface to form new functional groups, such as C–O, C=O, O=C–O or even more exotic groups [20]. On the other hand, O₂ plasma can produce more significant ablation of the rubber surface, which can result in the entire removal of the oil layer [21].

Although considerable efforts have been devoted to the studies of DLC/rubber adhesion, a comparative study on the effects of various plasmas on DLC/rubber adhesion has not been reported, which can be critical for selecting the appropriate plasma pretreatment.

Another important concern of DLC/rubber is their friction behavior. Generally, excellent friction performance can be achieved by avoiding the adhesive force by depositing inert DLC films, improving the adhesion between the DLC films and rubber, forming a high density of crack (small patch size), and generating a transfer layer during friction [22–25]. It is understandable that a smaller patch size has a lower probability of fracture during loading/sliding and endows DLC/rubber with better flexibility [26]. In addition, the effect of rubber roughness on the friction performance of DLC/rubber has been studied [27]. It was found that superior wear resistance can be obtained by depositing DLC films on rough/grainy rubber surfaces. By contrast, the relatively smooth rubber surface has a detrimental effect on the friction and wear performance of DLC/rubber [27]. Although the friction behavior has been extensively studied from the perspective of DLC films and rubber substrates, the relationship between plasma pretreatment and the friction performance of DLC/rubber is unclear.

In this work, the influence of different plasma pretreatment on the adhesion and friction behaviors of DLC films deposited on nitrile butadiene rubber (NBR) was studied, with the aim of identifying the optimal plasma pretreatment. The adhesion between the DLC films and NBR substrates was determined by applying the X-cut method [28] and scratch test using GCr15 steel balls (ø6 mm) as counterparts [29]. The friction performance of DLC/rubber was investigated via the ball-on-disk tribo-tests under 10 N loads to accelerate wear.

2 Experimental details

2.1 Sample preparation

A black NBR sheet of 2 mm thickness with Shore A

hardness of 80 ± 5 was provided by Northwest Rubber Plastics Research and Design Institute Co. Ltd. (Xianyang, China). Before the plasma pretreatment, the substrates were cleaned by soapy water and boiling water, and then dried under air flow. Plasma pretreatment of the NBR substrates and the deposition of DLC films were carried out via a plasma enhanced chemical vapor deposition (PECVD) system. The NBR substrates were placed on the substrate holder and transferred into the chamber, and then the vacuum chamber was pumped to 1.0×10^{-3} Pa. The deposition process consisted of three steps. First, the NBR substrates were etched by Ar plasma (300 sccm, -900 V, 15 min, and 5.8 Pa working pressure) to further remove surface contaminants. Second, oxygen (O_2), hydrogen (H_2), nitrogen (N_2), or Ar plasma were applied to improve the adhesion. In this step, the etching parameters (100 sccm, -900 V, 15 min, and 5 Pa working pressure controlled by throttle) were constantly maintained. Finally, the DLC films were deposited with the following parameters: applied dc-negative bias power voltage of -800 V, frequency of 60 kHz, duty cycle of 60%, and duration time of 120 min. The gas flowrate was set to $Ar/CH_4=15/10$ sccm, and the deposition pressure was kept constant at 20 Pa. The obtained samples were named as Ar-X/DLC, where X refer to the plasma treatment type in the second step. The pretreatment and deposition temperatures were strictly maintained at values below the upper limit ($150^\circ C$) of NBR with a water cooling system, and the temperature fluctuation was measured with a surface thermometer.

2.2 Sample characterization

The morphology (surface and cross-sectional) of DLC/rubber was characterized by using a scanning electron microscope (ThermoScientific™ Apreo S, SEM). The cross sections of DLC/rubber were made by fracturing the specimens after cooling in liquid nitrogen for 10 min. The cross-sectional profile was analyzed by using a 3D surface profilometer (ZYGO Nexview, USA). Raman spectra were acquired to investigate the chemical

bonding of the DLC films by using a HORIBA Jobin Yvon S.A.S spectrometer at an excitation wavelength of the 532 nm Ar laser line and with a spot size of $5 \mu m$. The integration time was 20 s, and 3 accumulations were collected. The chemical state of the plasma-treated NBR samples was characterized by Fourier transform infrared spectroscopy (FTIR, Nexus 870) and X-ray photoelectron spectroscopy (XPS, PHI-570) with Al K α radiation as the excitation source.

In order to reliably determine the adhesion of DLC/rubber, the X-cut method was used to evaluate the adhesion levels. An “X” was cut into DLC/rubber with a blade, in which the angle of the two crossed lines was approximately $30\text{--}45$ degrees. A cellophane adhesive tape (Scotch® with adhesion to steel of 47 N/100 mm widths) was carefully adhered to the dissected film surface under a 10 N load. After 2 min, the tape was pulled off rapidly (not jerked). The peeling off or delamination of the film at X-cut area was observed by SEM [28]. The adhesion levels of DLC/rubber were quantitatively assessed by using a scratch tester, in which GCr15 steel balls ($\phi 6$ mm) were used as counterparts. The test method was determined to be suitable for hard coating/soft substrate materials by Kaczorowski and Gajewski [29]. The scratch tester was an MFT-4000 multi-functional tester for material surface properties, which was manufactured by Lanzhou Huahui Instrument Technology Co. Ltd. (Lanzhou, China). The applied force linearly increased from 5 to 100 N over a distance of 10 mm. The magnitude of the adhesion strength was comprehensively determined based on the SEM images and acoustic sign.

The friction performance of DLC/rubber was determined at room temperature ($23^\circ C$) using an in-house tribo-tester with the rotating ball-on-disc configuration and commercial $\phi 6$ mm GCr15 steel balls as counterparts. The parameters of the friction tests were as follows: the friction load was 10 N, the linear speed was 83.73 mm/s, the radius of rotation was 4 mm, the testing time was 60 min, and the relative humidity was maintained at $25\% \pm 1\%$ with a humidity regulator. All the

tribo-tests were carried out at least three times to ensure repeatability.

3 Results and discussion

3.1 Surface morphology of virgin and pretreated NBR

Figure 1 shows the SEM micrographs of NBR without and with different plasma pretreatment. The surface of virgin NBR (after cleaning by soapy water and then boiling water) was covered by a smooth layer, as shown in Fig. 1(a), indicating that an aqueous soap solution is insufficient in removing wax and contaminants. Therefore, in the early stage of the treatment process, Ar plasma was chosen to remove the contaminants (at the molecule level) on the NBR surface, and decrease the influence of impurities on the subsequent plasma treatment. Pitted areas and holes with diameters of 200 nm were found on the NBR surface after 15 min of Ar plasma cleaning (Fig. 1(b)), indicating that Ar plasma can remove the adherent layer and strip the virgin rubber "skin". It should be noted that the role of Ar plasma is to transfer energy from the plasma towards the rubber surface (bombardment effect), and there is no chemical reaction between the Ar plasma and NBR [14]. In addition, the thermal effect caused by 15 min of Ar plasma discharge is negligible as the

temperature only reaches 43 °C.

The plasma in the second treatment stage has a significant effect on the morphology of the NBR surface (Figs. 1(c)–1(f)). Evidently, the rubber surface is degraded after the O₂ plasma treatment (Fig. 1(c)). In contrast to the Ar plasma, the radicals in the O₂ plasma may react with the additives and molecular chains of rubber [21]. Both chemical reactions and etching can accelerate the deterioration of the NBR surface and promote the formation of vertical spikes and fine voids on the surface. Compared with the Ar–O₂ plasma treatment, the damage to the rubber surface by the Ar–H₂ plasma is slighter. A rounded scaly sheet and homogeneous dispersion of holes of 50 nm in diameter are presented (Fig. 1(d)). An interesting phenomenon is the occurrence of bright particles grafted on the scaly sheet (Fig. 1(d)), which may be attributed to the chemical reactions involving the positive ions of the hydrogen plasma and the free radicals and chain molecules of the rubber surface [19]. In the case of Ar–N₂ plasma treatments, a fine globular texture was observed on the NBR surface (Fig. 1(e)), attributable to the scission of rubber chains by the nitrogen plasma to increase the surface crosslinking of short chains. NBR treated with the Ar–Ar plasma resulted in a relatively homogeneous and smooth surface (Fig. 1(f)). As the Ar plasma treatment time increased (compared to Fig. 1(b)), the loose nanostructure changed to a

Fig. 1 Surface morphologies of NBR with different plasma pretreatments: (a) no pretreatment, (b) Ar plasma cleaning for 15 min, (c) Ar–O₂, (d) Ar–H₂, (e) Ar–N₂, and (f) Ar–Ar.

compact configuration, which may be attributed to the transfer of energy from the Ar plasma to the NBR surface, thereby promoting the formation of free radicals and atomic migration [30]. From the SEM results, it can be inferred that oxidation reactions are initiated from the NBR surface under O₂ plasma conditions. Furthermore, Ar plasma can promote the formation of free radicals at or near the NBR surface, which can convert low-molecular-weight residues to high-molecular-weight residues by crosslinking reactions.

3.2 Composition and structure of virgin and pretreated NBR

The chemical structures of the virgin and plasma-treated surfaces were characterized by FTIR spectroscopy. As shown in Fig. 2, there are three characteristic peaks at 2,917, 2,848, and 1,438 cm⁻¹, corresponding to the –CH₂– nonsymmetry stretch vibration, –CH₂– symmetry stretch vibration, and –CH₂– non-symmetry changing angle vibration, respectively. It is known that the wax used in rubber manufacturing mainly contains these groups [31]. After the samples were treated with different plasma, the peak intensity of these groups in the FTIR spectra remarkably decreased, when compared with that of virgin NBR. The result confirms that plasma treatment can remove wax from the NBR surface, especially with Ar plasma and O₂ plasma treatments. Furthermore,

the peaks at 2,235, 1,168, 961, and 917 cm⁻¹ were respectively assigned to the C≡N expansion vibration of unsaturated nitrile, C–H in plane stretching vibration, the C–H deformed vibration of two substituted alkenes, and the C–H deformation vibration of mono substituted alkenes, representing the typical characteristic peaks of NBR [31]. Clearly, the Ar–H₂ plasma-treated NBR surface displays the strongest intensities for the above peaks, indicating that this surface contains the greatest number of C–H bonds.

Further, it was found that significant changes in the spectra occurred at 1,500–1,747 cm⁻¹, which contains the C=O stretch absorption at 1,730 cm⁻¹ and the COO– asymmetrical stretch absorption at 1,650–1,560 cm⁻¹ [10]. It can be seen that, except for the oxygen plasma-treated NBR, the intensities of the oxygen-based vibration peaks of the Ar, N₂, and H₂ plasma-treated NBR are lower than that of the virgin NBR. In addition, according to Fig. 1(c) and the peaks in the spectral range of 1,650–1,560 cm⁻¹ (Fig. 2), it is likely that two processes simultaneously occur during the oxygen plasma treatment: the formation of oxygen-containing functional groups on the NBR surface and the generation of volatile products. Overall, the recorded FTIR spectra for all the samples do not reveal any significant differences, except in the narrow spectral range of 1,650–1,560 cm⁻¹. It is reasonable to conclude that modifications occur during cleaning and plasma irradiation, which resulted in the formation of free radicals and subsequent crosslinking.

To more accurately determine the chemical composition of the NBR rubber after plasma modification, XPS studies were performed. Figure 3 shows the XPS survey scan spectra of NBR before and after different plasma treatments. It is evident that the spectra consist peaks arising from carbon (C1s), nitrogen (N1s), and oxygen (O1s) at 284, 396.5, and 532 eV, respectively. In addition, weak peaks due to zinc (Zn2p) were observed, which is in good agreement with the composition of NBR. The oxygen contents (O/C ratios) of the plasma-treated NBR is higher than that of the virgin NBR, which can be ascribed to

Fig. 2 FTIR spectra of NBR rubber before and after the different plasma treatments.

the formation of oxygen-containing functional groups via the reaction of carbon radicals with oxygen molecules (O_2 and H_2O) when the samples are exposed to ambient air [32]. The different oxygen content may be used to qualitatively indicate the number of carbon radicals on the NBR surface resulting from the different plasma pretreatment. However, the increase in oxygen content upon oxygen plasma exposure is mainly attributed to the reaction of the O_2 plasma with NBR. Another peculiar phenomenon is that an extremely small quantity of nitrogen (low N/C ratios) was incorporated on the NBR surface during the N_2 discharge period. We believe that the affinity between the nitrogen-containing species and carbon radicals on the NBR surface is low (Fig. 3), and that low oxygen contamination may strongly hamper the incorporation of nitrogen on the NBR surface.

Considering that the adhesion between the DLC films and NBR substrates is dependent on the chemical structure of the NBR surface, the two regions of the spectrum, namely C1s and O1s, were further subjected to detailed analysis. Figures S1 and S2 in the Electronic Supplementary Material (ESM) show the high-resolution XPS spectra in the C1s and O1s regions of NBR before and after different plasma treatments. The C1s spectrum can be fitted to three components corresponding to C–C/C–H (284.8 eV), C–N/C–O (285.8 eV), and O=C–

O/O=C–N (288.3 eV), respectively. The proportion of the C–C/C–H component is significant and most likely originated from the hydrocarbon backbone of NBR [30]. H_2 plasma was found to promote the increase in the C–C and C–H bonds, which can be attributed to the incorporation of hydrogen atoms on the NBR surface (Fig. S1 in the ESM). Moreover, an evident change in the ratio of the C–N/C–O and O=C–O/O=C–N peak was observed, where the ratios for the different plasma-treated NBRs are greater than that of virgin NBR (Fig. S1 in the ESM). Notably, the ratio of C–N/C–O is the highest in the NBR treated with the Ar–Ar plasma (Fig. S1 in the ESM), which indicates that Ar plasma is the most effective at subtracting hydrogen and forming carbon free radicals at or near NBR surface, thus facilitating the deposition of DLC films.

The deconvolution of the O1s band (Fig. S2 in the ESM) revealed three peaks, which were assigned to C–O–C (533.2 eV), C–OH/C=O (532.2 eV), and Zn–O/O=S=O (530.6 eV). For all the plasma-treated samples, the Zn–O/O=S=O peak exhibited the most significant change when compared with that of virgin NBR (Fig. S2 in the ESM). This suggests that plasma treatment is effective at removing the sticky layer on the NBR surface. Meanwhile, plasma modification also acts to expose a large amount of fillers from the bulk to the rubber surface, which may have an adverse effect on the deposition of DLC films deposition. Therefore, according to the area of the Zn–O/O=S=O peak, more fillers are exposed on the NBR surfaces treated with oxygen and nitrogen plasma (Fig. S2 in the ESM).

3.3 Surface morphology of DLC/rubber

The surface morphologies of the DLC/rubber specimens are shown in Fig. 4. As can be seen from the low-magnification images, the stripe-like and uneven granular morphology is remarkable in Ar– O_2 /DLC (Fig. 4(a)). By contrast, stripe-like and patch-like morphologies were observed for the other DLC/rubber specimens (Figs. 4(c) and 4(d)). The stripe-like morphology is attributed to the injection molding used in the NBR manufacturing process. The patch-like morphology is a typical

Fig. 3 XPS wide scan spectra of NBR rubber before and after the different plasma treatments.

Fig. 4 Microstructure of DLC/rubber with different plasma pretreatments: (a) Ar–O₂, (b) Ar–H₂, (c) Ar–N₂, and (d) Ar–Ar. **Top:** lower magnification (scale bar: 500 μm); **bottom:** higher magnification (scale bar: 5 μm).

feature of hard coatings deposited on soft or flexible substrates, which is induced by the huge difference in the thermal expansion coefficient and elasticity between the DLC films and NBR substrates. However, it can be seen that the surface of Ar–O₂/DLC contains a few cracks, attributable to the formation of voids on NBR after the Ar–O₂ plasma treatment (Fig. 1(c)). Furthermore, the density of the crack network is similar for DLC/rubber with Ar–N₂, Ar–H₂, and Ar–Ar plasma pretreatments (Figs. 4(b)–4(d)). Consequently, the effect of the crack network density on the adhesion and friction performance of DLC/rubber is negligible in the follow-up discussion.

At high magnification, it can be seen that the Ar–O₂/DLC film has the loosest and grainiest morphology (Fig. 4(a₁)). It is likely that the vertical spikes and fine voids on the surface of the NBR with the Ar–O₂ plasma treatment greatly influence the nucleation and impingement of carbon atoms during the deposition of DLC films (Fig. 1(c)). The DLC films prepared on the other plasma-treated NBR surfaces are relatively compact (Figs. 4(b₁)–4(d₁)) with a network of grooves, where the micron valley structure may store debris during friction. Notably, the uneven granular structure divided by a gap of tens of nanometers is expected to enhance the strain tolerance and flexibility of Ar–O₂/DLC. However, the DLC films may not protect the NBR matrix, because the NBR substrates can directly contact external impurities via the gap.

3.4 Cross-sectional profile analysis

The fractured cross-sections of DLC/rubber are shown in Fig. 5. The fractured cross-sectional morphology of Ar–O₂/DLC contains a loose and columnar microstructure (Fig. 5(a)), which may be related to the voids on the NBR surface (Fig. 1(c)) hindering the continuous growth of DLC films. In the case of Ar–H₂/DLC, the fractured cross-sectional morphology clearly reveals the formation of defects. Although it is common that numerous C–H bonds are formed by passivation, adhesion can be improved by dehydrogenation during film deposition [15]. However, these interface holes indicate that this was not achieved (Fig. 5(b)), which can be explained by the ocean of H ions on

Fig. 5 Fracture cross-sections of DLC/rubber with different plasma pretreatments: (a) Ar–O₂, (b) Ar–H₂, (c) Ar–N₂, and (d) Ar–Ar.

the rubber surface at the beginning of the deposition process (Fig. S1 in the ESM), hindering dehydro-genation for a short time and thus holes are formed via bridges. In the case of Ar–N₂/DLC and Ar–Ar/DLC, the interface between the DLC films and rubber is compact, which can be correlated to the free radicals and surface topography after plasma pretreatment (Figs. 5 (b) and 5(d)).

A section analysis is conducted by drawing a cross-sectional line across the pretreated rubber and DLC/rubber surface, as shown in Fig. 6. The roughness value of the NBR with the Ar–O₂ plasma pretreatment is higher than that of the virgin rubber surface, whereas the roughness values of the NBR with the other plasma pretreatments are lower than that of the virgin rubber surface (Fig. 6(a)). This can be attributed to the large number of voids formed on the rubber surface after the oxygen plasma pretreatment (Fig. 1(c)), while the other plasmas removed impurities and promoted crosslinking for a smoother rubber surface. Compared with the roughness of the plasma-pretreated rubber, the surface roughness of the corresponding DLC/rubber is reduced. This can be explained by the shadowing model of columnar growth, which is initiated from the rough surface where carbon atoms are accumulated in the holes embedded in the rubber surface [19]. In particular, it should be noted that the amplitude of the cross-sectional profile of Ar–Ar/DLC is significantly enhanced when compared with the Ar–Ar plasma-treated rubber surface profile, but the average roughness is relatively low (Fig. 6). From the section analysis (Fig. 6(a)), the Ar–Ar plasma-treated rubber surface is smooth and the distribution of fine holes is relatively uniform. According to the shadowing model of columnar growth, free radical carbon atoms will firstly accumulate in the holes to facilitate the formation of columnar structures [19]. A closer examination of the results indicates that the average roughness is almost the same for Ar–Ar/DLC, Ar–N₂/DLC, and Ar–H₂/DLC, whereas the vibration intensity of the cross-section line shows the following order: Ar–Ar/DLC > Ar–N₂/DLC > Ar–H₂/DLC (Fig. 6(b)). It must be pointed out that the fluctuations, presenting an approximate

sine function for Ar–Ar/DLC, have a huge impact on the friction performance of the sample, which will be mentioned later. Notably, the cross-sectional profile of Ar–O₂/DLC deviates from the morphology of the fractured cross section (Fig. 5(a)), which can be attributed to the scanning range and accuracy of the measurement. The scanning range in Fig. 5(a) is only 6 μ m, while the scanning range of the three-dimensional profile is 1.0 mm (Fig. 6(b)). Therefore, the columnar structure surfaces are not reflected in the optical 3 dimensional (3D) surface profilometry due to the nanoscale voids. Further, we provide a small range (0.1 mm) of the cross-sectional profile (Fig. S3 in the ESM), and find that the profile curve is closer to the topography of Ar–O₂/DLC (Fig. 5(a)).

Fig. 6 Cross-sectional profile of (a) untreated and plasma-treated NBR and (b) DLC/rubber with different plasma pretreatment.

3.5 Raman analysis of DLC/rubber

Raman spectroscopy is an effective and nondestructive tool to characterize the detailed bonding structure of DLC films. The full spectra of DLC/rubber with various plasma pretreatments are shown in Fig. 7(a), consisting of the prominent G and smaller underlying D peaks (centered approximately 1,530 and 1,350 cm^{-1} , respectively). The G-peak is attributed to the stretching vibration of the sp^2 bonds in chains or in aromatic rings, and the D-peak is assigned to the breathing mode of the sp^2 bonds in the rings only [33, 34]. Generally, more information on the carbon bonds can be derived by the deconvoluted data including the G-peak position and the intensity ratio of the D to G peaks (I_D/I_G), where the G-peak position is considered to depend on the sp^2 content and the I_D/I_G ratio has a direct correlation with the sp^2/sp^3 ratio.

The variation of the fitted G-peak position and I_D/I_G values of DLC on the various plasma-pretreated NBR are depicted in Fig. 7(b). There is no obvious change in the G peak position ($1,527 \pm 2 \text{ cm}^{-1}$) and I_D/I_G ratio (0.44 ± 0.03) for Ar- N_2 /DLC, Ar- H_2 /DLC, and Ar-Ar/DLC, which suggests that the microstructure of the DLC films was not influenced by the N_2 , H_2 , and Ar plasma pretreatments. However, the G-peak position and I_D/I_G ratio of Ar- O_2 /DLC are higher than those of the other samples. This may be attributed to the growth of the film in irregular patterns, increasing the sp^2 content through carbon agglomeration [35]. The granular surface topography of the Ar- O_2 plasma-treated rubber results in a decrease in diffusivity of carbon on the rubber surface, which further leads to the formation of sp^2 -bonds by carbon agglomeration. Moreover, the irregular coating may be attributed to the poor bonding between the NBR substrates and carbon particles due to the limited activation sites. The poor bonding may lead to an increased affinity between the carbon-carbon particles during the deposition process, increasing the sp^2 bond content. Therefore, the results confirm that the type of plasma pretreatment has little effect on the microstructure

Fig. 7 (a) Raman spectra and (b) I_D/I_G and G peak position of DLC/rubber with various plasma pretreatments.

of the DLC films, although the surface topography of the rubber substrates is affected.

3.6 Adhesion

To examine the interfacial adhesion strength of DLC/rubber with different plasma pretreatments, the X-cut method and scratch tests were performed. Figure 8 shows the SEM images of the X-cuts after the peeling tests. Although adhesion cannot easily be assessed by the X-cut incision, the pattern on the adhesive tape of the X-cuts (upper right corner of each corresponding image) can be used to qualitatively distinguish the adhesion strength. Film peeling occurs at the incision and edges on the Ar- O_2 /DLC surface, and trace peelings appear in the incisions on the Ar- H_2 /DLC surface (Figs. 8(a) and 8(b)). However, it is difficult to distinguish the adhesion strength of Ar- N_2 /DLC and Ar-Ar/DLC because both display incisional marks. Moreover, the film at the edge of the incision is distinctly not attached to the tape (Figs. 8(c) and 8(d)). Evidently, the adhesion strengths of Ar- N_2 /DLC and Ar-Ar/DLC are much higher than

those of Ar–O₂/DLC and Ar–H₂/DLC. Based on the above observations, it can be concluded that the choice of adhesive tape is particularly critical and the use of tape is limited in the determination of the adhesion strength. Therefore, the adhesion strength of the samples is further studied in the following tests.

Table 1 shows the scratch test data for DLC/rubber with different plasma pretreatment, where the surface image and acoustic sign obtained after the scratch tests are presented in Fig. S4 in the ESM. Two critical loads were determined: the lower critical load (Lc1) causes the film to tilt up and the upper critical load (Lc2) damages the DLC films from the NBR surface. The values of Lc1 and Lc2 are respectively 21.26 and 63.68 N for the Ar–Ar/DLC and 20.43 and 50.25 N for Ar–N₂/DLC. Therefore, the adhesion strengths of all the films can be arranged as follows: Ar–Ar/DLC > Ar–N₂/DLC > Ar–H₂/DLC > Ar–O₂/DLC.

The adhesive strength is significantly affected by the plasma modification of the NBR substrates.

Fig. 8 SEM images of X-cuts after peel tests for DLC/rubber with different plasma pretreatments: (a) Ar–O₂, (b) Ar–H₂, (c) Ar–N₂, and (d) Ar–Ar.

Table 1 Comparison of the adhesion of DLC/rubber with different plasma pretreatments.

DLC/rubber	Critical load Lc1 (N)	Critical load Lc2 (N)
Ar–O ₂ /DLC	5.14	12.87
Ar–H ₂ /DLC	12.60	24.30
Ar–N ₂ /DLC	18.43	50.25
Ar–Ar/DLC	21.26	63.68

Although O₂ plasma is capable of removing organic contaminants [36], it further reacts with the rubber matrix to deteriorate the rubber surface, i.e., creating a surface morphology of vertical spikes and fine voids (Fig. 1(c)). This morphology prevents the DLC films from fully contacting the rubber, resulting in segmentation-like columnar growth of the DLC films and poor adhesion. Similarly, the H₂ plasma pretreatment failed to enhance adhesion, even though the treatment was designed to promote the formation of C–H bonds and induce dehydrogenation at the beginning of the film deposition to improve adhesion. However, dehydrogenation was not achieved in the short DLC deposition time, resulting in the formation of a large amount of voids at the interface between the DLC film and NBR substrate (Fig. 5(b)). The N₂ plasma was not as effective as the Ar plasma at improving adhesion, which can be attributed to the increased surface crosslinks between fragile short chains and the large amounts of fillers exposed on the rubber surface (Fig. S2 in the ESM). The Ar plasma treatment is the most effective at enhancing adhesion. Plasma based on noble gases (e.g., He or Ar) are effective at creating free radicals on the NBR surfaces. The free radicals produced by the Ar plasma can only link other surface radicals or other chains in chain-transfer reactions [37]. Therefore, it can be deduced that the increased adhesion strength of DLC/rubber is related to the removal of organic contamination and weak boundary layers, and the formation of free radicals.

To further investigate the relationship between adhesion and carbon free radicals, we measured the water contact angle to indirectly account for the changes in free radicals, because a greater free radical content produces a higher surface energy which is manifested in the formation of small water contact angles [38]. Figure 9 shows the optical image of a water droplet on the surfaces of virgin NBR and different plasma-pretreated NBR samples. The order of contact angle was found to show an opposite trend with adhesion strength, indicating that carbon free radicals play a key role in adhesion (Fig. 9). In addition, the contact angle

Fig. 9 Optical image of a water droplet on the surface of NBR. (a) Without pretreatment and with different plasma pretreatments: (b) Ar-H₂, (c) Ar-Ar, (d) Ar-N₂, and (e) Ar-O₂.

of NBR with water is greatly reduced after the Ar-Ar plasma treatment (Fig. 9(c)), indicating that the Ar plasma facilitates the generation of carbon free radicals, in agreement with the XPS results (Fig. S1). Notably, the wettability of rubber changed after the O₂ plasma treatment, from a hydrophilic surface to a hydrophobic one, which may be attributed to the surface morphology of vertical spikes and fine voids.

3.7 Friction performance

The evolution of the friction coefficient (CoF) as a function of the sliding cycles of virgin NBR and DLC/rubber with different plasma pretreatments is shown in Fig. 10. The deposition of DLC films significantly reduced the CoF, attributable to the chemical inertness of the DLC films, which separates the rubber molecules from the counterparts. The friction curve of Ar-Ar/DLC achieved a steady state, whereas a continuous growth in CoF was observed for the other curves. The trend of the average CoF (Fig. 10 insert) is consistent with that for the adhesion of DLC/rubber with different plasma pretreatments. Therefore, excellent adhesion may ensure that DLC films exhibit stable performance in a sustained friction test. For Ar-O₂/DLC, the initial

CoF was as low as 0.20 and instability increased with the sliding time (Fig. 10). By the end of the test, the CoF reached a relatively high value of 0.52. The instability in the friction curve together with the gradual increase in the CoF indicates a gradual damage of the DLC films. In addition to the poor adhesion, the deteriorating mechanical strengths of the rubber surface and DLC films contribute to the poor friction performance of Ar-O₂/DLC. The friction curves of Ar-H₂/DLC and Ar-N₂/DLC show an upward trend, indicating that the DLC films are still functional. This may be related to the viscoelastic characteristics of the plasma-pretreated rubber, resulting in variable sizes of the contact area between the counterpart ball and the DLC films. Notably, the higher slope of the friction curve growth of Ar-H₂/DLC is a direct result of poor adhesion, causing the edges of the sharp cracks to tilt up and exert additional resistance against the counterpart. The increase in CoF of the DLC/rubber with N₂ plasma pretreatment may also be associated with the irregular surface profile of the DLC films. The Ar plasma pretreatment is the most effective at improving the friction properties of DLC/rubber. The friction curve with a slope of almost zero is an indicator that the film maintained steady state conditions and does not

Fig. 10 CoF of virgin NBR and DLC/rubber with different plasma pretreatments.

suffer much damage. The greatest friction performance was observed for Ar–Ar/DLC, which can be explained as follows: (1) The sharp banks of the cracks extend into the interior of the rubber due to the excellent adhesion (as shown in Fig. 4(d₁)), which results in blunted banks and thus a decrease in the friction force. (2) The formation of concave (“valley”) and convex (“hill”) features on the Ar–Ar/DLC surface seems to have a positive influence on its frictional characteristics. The approximate sin function fluctuation mode (as shown in Fig. 6(b)) can reduce the contact area during the tribo-tests, which in turn reduces the adhesive contribution to friction, resulting in a stable CoF. (3) The Ar plasma pretreatment facilitates the formation of a compact layer on the rubber surface (Fig. 1(f)), and thus the NBR surface becomes stiffer and the viscoelastic contribution to friction is reduced. Therefore, the decrease in the adhesive interaction and hysteresis contribution lays a foundation for superior friction performance.

The wear tracks formed on DLC/rubber with different plasma pretreatments are illustrated in Fig. 11. The discrete columnar structures in Ar–O₂/DLC are seriously damaged after the tribo-tests, even though they appear to adhere to the substrate (Fig. 11(a)), indicating that the O₂ plasma cannot enhance the adhesion of DLC/rubber and the load bearing capability is weakened. In addition, the broken particles at the periphery of the patch-like structures are stored in

Fig. 11 Microscopic SEM images of the wear tracks of DLC/rubber with different plasma pretreatments: (a) Ar–O₂, (b) Ar–H₂, (c) Ar–N₂, and (d) Ar–Ar.

the wear tracks on Ar–H₂/DLC (Fig. 11(b)). The crack edges that are bent outwards are likely the main source of debris. However, the wear tracks of Ar–N₂/DLC and Ar–Ar/DLC are hardly visible at low magnification (Figs. 11(c) insert and 11(d) insert). Closer observations reveal that some of the tiny smooth plates are abraded and polished by the counterparts. Therefore, the segmented structure and uneven films suppress the generation of wear particles, and the worn areas only occur at the top of the patches. The significant wear and the rise of CoF of Ar–N₂/DLC, compared with Ar–Ar/DLC, can be attributed to the irregular surface morphology of the DLC films and the granular surface structure on the N₂ plasma-pretreated NBR. In addition, the fine patch-like microstructure of the DLC films has been reported to impart DLC/rubber with excellent friction performance [17, 22]. The sizes of the patches are almost identical in our samples, except for Ar–O₂/DLC, and thus the effect of film flexibility on friction performance was not further considered.

4 Conclusions

The adhesion and friction performance of DLC/rubber with different plasma pretreatments were evaluated. Plasma treatments significantly affected the surface morphology and chemical property of the NBR surface. According to the

FTIR and XPS results, Ar plasma and O₂ plasma were proved to be effective at removing wax and contaminants on the rubber surface. However, O₂ plasma can continue to react with the molecular chains of rubber, contributing to the decline in the surface mechanical properties, adhesion, and friction performance of DLC/rubber. The adhesion of Ar–H₂/DLC is relatively low, which is considered as the main reason for the rise in CoF. The increase in CoF of Ar–N₂/DLC can be associated with the surface crosslinks between fragile short chains, the exposed fillers on the modified rubber surface, and the irregular surface profile of the DLC films. The optimum adhesion strength of 63.68 N was observed for Ar–Ar/DLC; this superb interfacial adhesion ensures the excellent friction performance of DLC/rubber. Furthermore, the observed stable friction curve is ascribed to the formation of a compact layer on the rubber surface after the Ar pretreatment and the formation of concave (“valley”) and convex (“hill”) structures on the Ar–Ar/DLC surface. Accordingly, the type of plasma used to modify the rubber surface prior to the film deposition plays an important role in the adhesion and friction performance of DLC/rubber. Moreover, the conditions of the DLC film deposition, including atmosphere components (i.e., ratio of mixture gas), pressure, ion incident energy, and plasma excitation source, significantly impact the adhesion and friction performance of DLC/rubber, which will be further explored in our future works.

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