

Modification of rubber surface with hydrogenated diamond-like carbon thin films

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ABSTRACT

Thin films of hydrogenated diamond-like carbon (DLC) have been deposited on hydrogenated nitrile butadiene rubber (HNBR) for reduction of friction and enhancement of wear resistance of dynamic rubber seals, by sputtering graphite targets in C_2H_2/Ar plasma. The wax removal and pre-deposition plasma treatment are proven to be crucial and effective for the improvement of film performance due to enhanced adhesion. The columnar structure and the crack network formed during deposition enhance the flexibility of DLC thin films and exhibit strain tolerance up to 5%. After stretched to 50% strain and being unloaded from the strained status, thin DLC films of ~ 300 nm thickness still adhere very well on the rubber substrates and no spallation or delamination has been observed. The optimized DLC thin film on plasma treated HNBR rubber exhibits very low coefficient of friction of 0.19 (compared to > 1 of uncoated HNBR rubber) at high normal load of 3 N and after being stretched to 50% strain.

Keywords: DLC thin film, magnetron sputtering, rubber substrate, flexibility, tribology

1 INTRODUCTION

Rubbers are widely used in various engineering applications. Nonetheless, rubbers exhibit very high friction when sliding against other materials. It is known that contact rubber seals are the major source of friction of lubrication systems or bearings, which may take 50-70% of the total friction loss. The high friction of rubbers is due to the adhesion-prone of rubber to the counterpart, the ploughing of asperities of harder counterpart (steel, glass, etc.) on the rubbers surface and the so-called "hysteresis" that relates to the viscoelastic nature of rubbers¹. Besides the high friction, wear of rubbers is usually severe and mostly relates to adhesive and abrasive wear. So far, there are two solutions that can be used to reduce the friction and to enhance the wear resistance of rubber components: lubrication and coating. As to the first solution, oil or grease is applied to improve the surface lubricity of rubbers. However, it has drawbacks such as the degradation of lubricants and environmental pollution problems. For the second solution, a layer of an appropriate wear-resistant material is coated on the working surfaces of rubber components in order to protect the rubbers from wear and to reduce the friction. The development of advanced deposition methods makes the coating solution very

promising. To coat rubbers, two problems have to be considered: (1) The deposition temperature must not exceed the maximum working temperatures of various rubber materials; (2) The use of chemical substance, especially the toxic ones, in cleaning rubbers before deposition should be limited to prevent pollution. For a good performance, a coating deposited on rubbers must have (1) strong adhesion to rubber substrates, (2) sufficient flexibility to adapt large strain of rubbers under applied loads and (3) good wear resistance and low friction. According to these criteria, efforts in finding appropriate coatings for rubbers lead to diamond-like carbon (DLC) and DLC-based thin films, which have been well investigated and industrialized for decades but mostly used on stiffer substrates such as metallic alloys or Si-wafers².

In this work, we deposit a thin layer of DLC (about 300 nm thickness) on rough HNBR rubber by sputtering of graphite targets in Ar/C_2H_2 plasma. Comparative study of tribology reveals that thin DLC films coated HNBR rubber may perform better than thick Me-DLC coated HNBR. The effect of magnetron enhancement is investigated on the film adhesion and tribological properties.

2 EXPERIMENTAL

Black hydrogenated nitrile butadiene rubber (HNBR) sheet of 2 mm thickness was used as substrate in this study. The HNBR substrates of 40×40 mm² size were first cleaned by soap in an ultrasonic cleaner then rinsed carefully with demineralized water. Thereafter, wax removal was carried out in ultrasonic tank with hot demineralized water (80-90°C). This washing process with hot water was repeated three times. After that the HNBR substrates were dried in a centrifugal machine and then heated up to 120 °C for 15 minute in order to evaporate all absorbed water. The substrates were cooled down in ambient air to room temperature before being loaded into the deposition chamber. The instrumental modulus of HNBR rubber, determined by the method described elsewhere³, is 15.2 MPa and its surface roughness is 0.35 μm measured after wax removal using laser confocal microscope.

Plasma etching pre-treatment of rubber substrates and deposition of DLC films were carried out in a Teer UDP400/4 closed-field unbalanced magnetron sputtering system, which was configured of four magnetrons evenly distributed along the round chamber of 400 mm diameter with two graphite targets opposite to each other (the other two magnetrons were powered off). HNBR substrates were etched in 250 kHz pulsed-DC Ar plasma at -400V bias

voltage for 20 minutes, and reached a temperature of 85°C at the end of plasma etching. The deposition process followed immediately after the plasma cleaning pre-treatment. DLC films were deposited by p-DC sputtering two graphite targets (99.9%) of dimensions of 249×133 mm² in Ar/C₂H₂ plasma, at 250 kHz and 75% duty cycle. The current applied on the graphite targets was fixed at 0, 0.2 and 0.8 A each, respectively, corresponding to average power of 0, 78 and 384 W. The gas flow rate was set at Ar/C₂H₂ = 15/10 sccm and the process pressure of 3×10⁻³ mbar was kept constant during deposition via throttle control. The HNBR substrates clamped 80 mm apart from the graphite targets were biased with pulsed DC (250 kHz, 75% duty cycle) at -200 V and the sample holder was rotated at a speed of 5 rpm. The deposition time varied in the range of 23–45 min to keep film thickness of 300 nm fixed. The maximum deposition temperature of each batch was measured in situ with a surface thermometer (model 574CM, PTC instruments, Los Angeles, USA).

Cross sections of the coated rubbers were made by fracturing after cooling in liquid nitrogen for ten minutes. The surface morphology, the cross section and wear track of uncoated and coated rubber after tribotests were characterized with scanning electron microscope (SEM) (Philips FEG-XL30). The film flexibility is estimated via stretch tests with a tensile stage inside the SEM. The coated rubber sheets were glued onto ø30 mm polished M2 steel discs for tribotests. The tests were performed at room temperature (23°C) on a CSM high temperature tribometer with ball-on-disc configuration. The counterpart was commercial ø6 mm 100Cr6 steel balls of hardness HRC 60–62. All the tribotests were carried out at sliding velocity of 10 cm/s and a constant humidity of 35±1 % kept with a humidity regulator

3 RESULT AND DISCUSSION

The surface morphology of DLC films coated HNBR is shown in Fig. 1. With increasing the p-DC current from 0 to 0.8A applied on each of the two graphite targets, the growth feature of the DLC films becomes finer and denser, as revealed in the SEM micrograph in the insets. This is attributed to the enhanced intensity of concurrent ion impingement during the growth of DLC films due to the enhanced flux of impinging Ar⁺ ions, where sputtering the graphite targets was operated at poisoning conditions. The steady deposition temperature also increases with increasing the sputtering current, from 66°C at 0A, 80°C at 0.2A to 115°C at 0.8A. Correspondingly, the temperature difference of HNBR substrates prior to and during deposition varies significantly, from -19°C, -5°C to 30°C. As a consequence, no crack network formed in the DLC thin films deposited with a magnetron current of 0A (magnetron off) and 0.2A, but instead fine wrinkles formed due to shrinkage of HNBR substrate during the onset of deposition (Fig. 1a and 1b), when the temperature dropped from 85°C at the end of plasma etching to the steady

deposition temperatures. In contrast, the DLC thin film deposited with 0.8A magnetrons current exhibits random cracks attributed to tensile stress in the onset of deposition developed with further rising of substrate temperature. It should be pointed out that the crack network is not harmful to the flexibility and tribological performance of coated rubbers, if the interfacial adhesion is satisfactory.

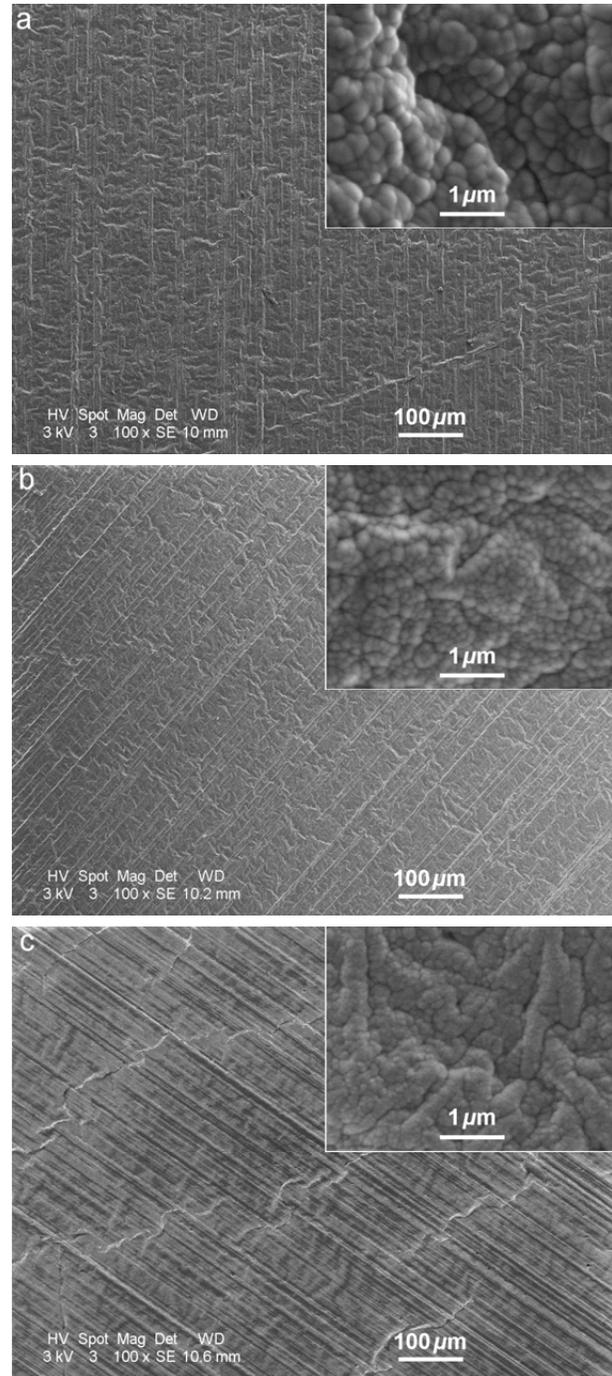


Figure 1: Surface morphology of DLC thin films on HNBR rubber deposited at magnetron sputtering current of: (a) 0A, (b) 0.2A and (c) 0.8A, respectively.

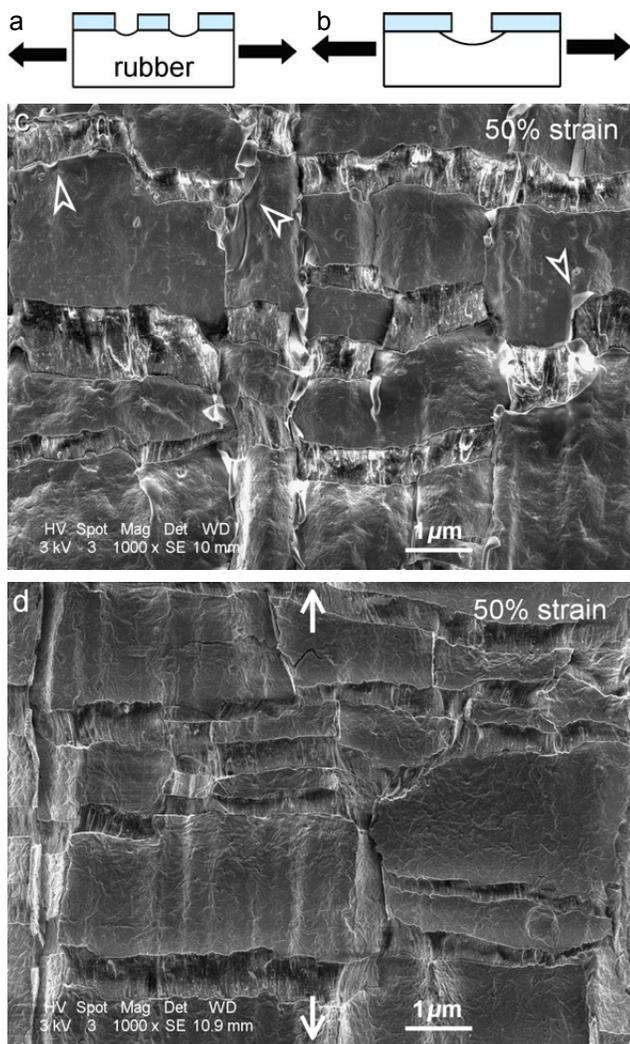


Figure 2: Sketch schematically showing the response of DLC thin film coated rubber with strong adhesion (a) and weak adhesion (b) under tension. Crack patterns of DLC thin films on HNBR deposited with 0.2A (c) and 0.8A (d) magnetron current, stretched to 50% strain along the direction indicated by a pair of arrows. The hollow arrows indicate the partial debonding of crack banks in (c).

Fracture pattern of thin films on flexible substrates such as rubbers may reflect their adhesion and flexibility. The fracture property and adhesion of DLC films coated HNBR rubber can be evaluated via tensile test. Fig. 2 presents the fracture pattern of thin films with different adhesion strength on the same rubber substrate. If the adhesion strength between a film and rubber substrate is strong enough, generation and opening of cracks are the only mechanism responsible for releasing the stress applied on the whole system. In this case, higher crack density can be observed on the film (Fig. 2a). If the adhesion is poor, beside the crack generation, debonding at the crack banks occurs to release the stress. Consequently, there are fewer cracks but with larger opening (lower crack density) (Fig. 2b). The effect of magnetron enhancement on the adhesion

strength of DLC thin films is clearly demonstrated by the result of tensile tests. Fig. 2c shows the crack patterns of DLC film deposited with 0.2A magnetron current, where partial debonding of crack banks are observed, as indicated by the hollow arrows. The degree of debonding is even heavier in the DLC film with magnetron powered off (not shown). In contrast, the DLC film deposited with 0.8A magnetron current exhibits excellent adhesion and no debonding is observed even when stretched to 50% strain. After being unloaded, the cracks are closed and no delamination can be seen. With measured crack spacing, film thickness and strength, the adhesion of DLC films may be readily estimated according to the analytical models⁴.

The tribological performance of a-C:H films coated HNBR rubber in comparison with that of thick W-DLC is shown in Fig. 3. The steady state is approached within the testing period of 10000 laps for all the DLC films coated HNBR samples. The coefficient of friction (CoF) of DLC films coated HNBR decrease with increasing the currents applied on graphite targets. Very low and stable CoF of about 0.17 is obtained when the current on graphite targets is 0.8 A. The CoF of 300 nm thick DLC film (plasma CVD, magnetron off) is almost the same as that of 1 μm W-DLC, about 0.22. The higher friction compared to that of other two DLC films (magnetron on) can be attributed to the lower hardness and poor adhesion of this film as mentioned previously. Although the CoF of this film is the lowest within the first 2000 laps, rapid increase of CoF is observed due to micro-chipping and delamination⁵. Applying a small current (0.2A) on the two graphite targets, the steady CoF of DLC film drops substantially and becomes more stable. After tribotest, the two DLC films with magnetron enhancement were intact and almost no obvious damage or wear was seen in the wear tracks.

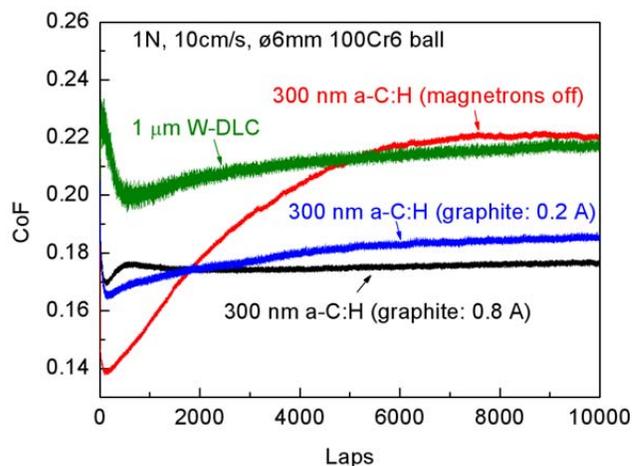


Figure 3: CoF of thin DLC films coated HNBR rubber under the tribo-test condition indicated, in comparison with that of 1 μm thick W-DLC coated HNBR.

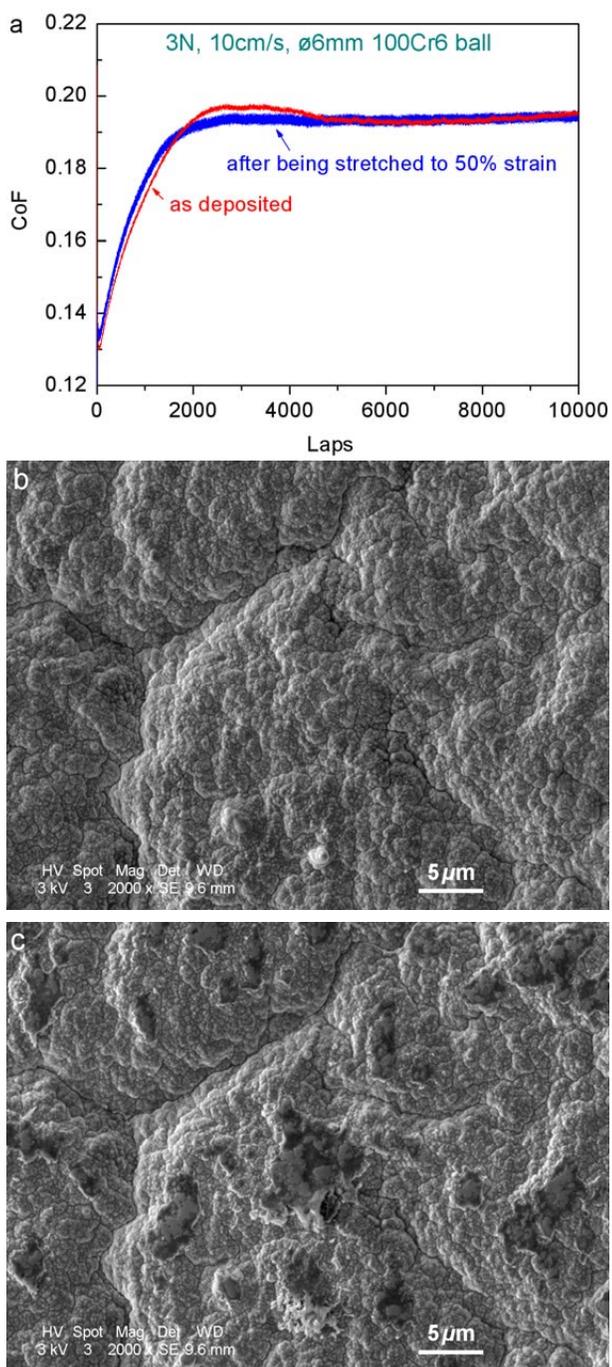


Figure 4: (a) CoF of an optimized DLC thin film on HNBR rubber as deposited and after being unloaded from 50% tensile strain, tested at 3N normal load and 10cm/s velocity. The surface morphology of an area at the center of the wear track on as-deposited film before (b) and after (c) tribo-test.

Fig. 4 shows the CoF of an optimized DLC thin film coated HNBR as-deposited and after stretch test up to 50% tensile strain, under tribo-testing condition of 3N normal load. It is remarkable that the CoF of stretched sample is almost the same as the CoF of as-deposited, except the thicker curve indicating slight fluctuation of friction due to

dense cracks formed during stretch test. This result confirms that the crack networks exert negligible influence on the frictional behavior of DLC thin films but contribute to the flexibility, on condition that the interfacial adhesion is strong enough so that no delamination may occur. The wear resistance of this film is very good, no damage but only mildly polished tiny spots can be seen on the “hills” of coated rubber after sliding of 10000 laps (Fig. 4c). The most part of the surface on the wear track is intact.

4 CONCLUSIONS

Thin DLC films have been deposited on rough HNBR rubber by sputtering of graphite targets in C_2H_2/Ar plasma. At -200V substrate bias voltage, magnetron sputtering enhances the interfacial adhesion of DLC films due to intensified concurrent ion impingement. The network of cracks and columnar structure make the DLC films flexible. After being stretched to 50% strain and unloaded, the DLC film deposited at 0.8A magnetron current still adhere very well on the rubber substrates and no debonding or delamination is observed. The DLC film deposited with magnetron off exhibits debonding at crack banks, indicating a weak adhesion. The coefficient of friction of the DLC films coated HNBR rubber considerably decreases with increasing magnetron current, from 0.22 to 0.17. Tribo-test result of optimized DLC film shows nearly identical CoF between the as-deposited film and after stretching to 50% tensile strain. The wear resistance of this thin film is excellent, even better than that of thick Me-DLC coatings on rubbers.

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