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Flexible diamond-like carbon film coated on rubber

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ABSTRACT

Dynamic rubber seals are major sources of friction of lubrication systems and bearings, which may take up to 70% of the total friction. The solution we present is to coat rubbers with diamond-like carbon (DLC) thin films by which the coefficient of friction is reduced to less than one tenth. Coating rubber is very challenging because the film must be flexible and strongly adhered to the surface of rubber substrate. Our novel approach is depositing flexible DLC films on rubbers via self-segmentation. By making use of the substantial thermal mismatch between DLC film and rubber substrates a dense crack network forms in DLC films and contributes to flexibility. The size of film micro-segments can be tuned by varying the bias voltage of pulsed-DC plasma CVD, which governs the amplitude of the substrate temperature variation during deposition. The formation mechanism of crack network and its effect on the flexibility and friction of DLC film coated rubbers are scrutinized. This paper provides generic design rules for the deposition of flexible and ultra-low friction DLC films on rubber seals.

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1. Introduction

Rubbers exhibit very high coefficient of friction (CoF) when sliding against most of the engineering materials (CoF=1–6), being the major source of friction in lubrication systems or bearings where dynamic rubber seals are widely used. The high friction of rubbers sliding against rigid solids is associated with contributions from interfacial adhesion and from energy losses in the bulk of the rubbers. By applying a chemically inert coating such as diamond-like carbon (DLC) film on rubber substrates, the interfacial adhesion between the sliding counterparts may be largely restrained [1,2]. For a rigid protective film deposited on compliant substrates such as rubbers, the most critical issues that determine the performance of the entire system are the film flexibility and interfacial adhesion. Sufficient flexibility of the protective film is required to adapt large deformation of rubber substrates under loading and can be achieved through film segmentation. Strong adhesion is a must that ensures the film segments adhering well on the rubber substrates and maintaining functionality under loading. In particular the combination of flexibility and strong adhesion is crucial for DLC films coated on dynamic rubber seals where cyclic and large elastic deformation may be exerted.

In the past a tile-like structure for films on rubber was proposed and deposited by using a net mask in front of the substrate [3]. Obviously, there are technical problems with this approach: the size of film segments is rather limited to sub-millimeter and especially the open gap of size at least tens of micrometers (equal to the thickness of the grid). Experimental results revealed that the impact between the asperity on the surface of sliding counterpart and the sharp edges of the open cracks in the films produced a large amount of debris that lead to a high friction and severe wear of coated rubber [2]. In this paper, we report another approach for depositing micro-segmented DLC films of superior flexibility on rubber. The novelty is that the size of film segments separated by close crack network can be well controlled at much smaller length scales. The formation mechanism of crack network during deposition and its effect on the friction of DLC film coated rubber are presented and reviewed [4].

2. Experimental

Hydrogenated nitrile butadiene rubber (HNBR) sheet of 2 mm thickness was used as substrate. The HNBR substrates of 45 mm × 45 mm size were first cleaned by detergent (Superdecontamine 33 from N.V. Intersciences S.A., Brussels) in an ultrasonic cleaner and then rinsed with demineralized water. Thereafter, wax removal was carried out in an ultrasonic tank with hot demineralized water (90–95 °C) [5]. This washing process with hot water was repeated three times. Next, the HNBR substrates were dried in

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Fig. 1. Evolution of measured substrate temperature vs. time of plasma cleaning (open symbols) and deposition (close symbols) with the solid curves fitted according to Eq. (1): (a) temperature drop (negative ΔT) and (b) temperature increase (positive ΔT) during deposition.

a centrifugal machine and then heated up to 120 °C for 15 min 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 is 10.2 MPa and its surface roughness is 0.35 μm measured after wax removal using laser confocal microscopy. The HNBR has a typical coefficient of thermal expansion $180 \times 10^{-6} \text{ K}^{-1}$.

Plasma cleaning 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 that were all powered off. HNBR substrates were cleaned by Ar plasma for 30, 35, 40 and 45 min at pulsed-DC (250 kHz, 87.5% duty cycle) bias voltage of -600 V , -500 V , -400 V and -300 V , respectively. During the last 10 min of plasma cleaning, hydrogen gas was added (50%) for reactive plasma cleaning to enhance the interface adhesion of DLC films. Immediately after the plasma cleaning treatment, DLC films were deposited by plasma CVD (p-CVD) at pulsed-DC bias voltage of -300 V and

Fig. 2. Surface morphology of DLC films on HNBR deposited at different temperature variations: (a and b) positive ΔT and (c and d) negative ΔT of values indicated.

–400 V, respectively, for 120 min and 60 min to reach the same film thickness of 300 nm. The ratio of gas flow rates was set at Ar:C₂H₂ = 3:2, and at constant process pressure of 3×10^{-3} mbar. However, the residual hydrogen in the inlet pipeline used also for acetylene might last till the first 10 min of deposition, during which period the growth of DLC film was only minor. The HNBR substrates were rotated at a revolving speed of 3 rpm during the deposition. The substrate temperature during plasma etching/deposition was measured in situ with a thermal couple inserted into the rubber sheet substrate.

The flexibility and adhesion strength of the DLC film were examined via in situ stretch tests on coated specimens of gauge section dimensions 10 mm × 3 mm × 2 mm, with a tensile stage installed in a Philips XL-30 FEG scanning electron microscope (SEM). The coated rubber sheets were glued onto ø30 mm polished M2 steel discs for tribotests. The tests were performed at room temperature (20–23 °C) on a CSM tribometer with ball-on-disk configuration. The counterpart was a commercial ø6 mm 100Cr6 steel ball of hardness HRC 60–62. All the tribotests were carried out at a sliding velocity of 10 cm/s and a constant humidity of $35 \pm 1\%$ kept with a humidity regulator. The surface morphology and wear track of DLC film coated rubber after stretch and tribotests were characterized with SEM.

3. Results and discussion

The measured temperature evolution of rubber substrates during plasma cleaning and successive deposition is shown in Fig. 1. The temperature variation (ΔT) of HNBR substrates during deposition is related to the bias voltage used for the p-CVD process and the substrate temperature at the beginning of deposition. Assuming that the plasma can be considered as a ‘hot body’ whose temperature (T_{plasma}) is constant and merely dependent on the bias voltage applied. The heat flow from the “hot” plasma to the “cold” substrate, which changes the temperature of substrate as a result, depends on the temperature differences between the plasma and the substrate. From Fourier’s heat conduction equation the temperature of a rubber substrate under plasma radiation follows

$$T = (T_0 - T_{\text{plasma}}) \times e^{-Kt} + T_{\text{plasma}} \quad (1)$$

where T_0 is the initial temperature of rubber substrate prior to deposition. The measured substrate temperatures vs. time of plasma treatment (cleaning and deposition) can be well fitted by Eq. (1), as indicated by the solid curves in Fig. 1.

The surface morphology of DLC thin films on HNBR deposited at varying substrate temperature is characterized by crack networks, as shown in Fig. 2. The effective temperature variation exposed during deposition governs the expansion or shrinkage of rubber substrates and thus the mismatch stress in a growing DLC film, which determines in turn the spacing of the crack network or the size of DLC film segments. It is understood that a positive ΔT or tensile stress in the growing DLC film leads to the formation of crack network once the stress is beyond the strength of DLC film and that the size of film segments is related to the amplitude of ΔT (see Fig. 2a and b). In contrast, a negative ΔT or compressive stress results in the formation of wrinkles and, due to bending fracture, also leads finally to a crack network whose density is likewise governed by the amplitude of ΔT (Fig. 2c and d). It is significant to realize that the crack network forms from the beginning of film deposition and propagates upwards together with the growth of DLC films as long as the stress is beyond the strength of DLC film, while the temperature of rubber substrates continuously changes during the entire deposition process. The surface morphology of film segments reflects

Fig. 3. Fracture cross sections of DLC films coated HNBR showing the profile of DLC film segments: (a) flat segments formed under tensile stress ($\Delta T = 3^\circ\text{C}$) and (b) convexly curved segments deposited under compressive stress ($\Delta T = -46^\circ\text{C}$). In both the cases, the edge of the segments bends inwards. (c) A close-up view of typical fracture cross-section of the DLC film coated HNBR.

on the different states of deformation: the film segments formed under tensile stress (positive ΔT) are rather flat (see Fig. 3a), and those generated under continuous compression (negative ΔT) are convexly curved as shown in Fig. 3b. It is noteworthy that, in both the cases, the edge of all the segments bends inwards and thus forms a crack-groove network. Such the geometry of crack-groove network surrounding the DLC film segments is attributed to the final shrinkage of rubber substrate as it cools down to room temperature after finishing of a deposition, which pushes the film segments against each other and bend inwards along the edge where the highest compressive strain is exposed. It must be

Fig. 4. Size of DLC film segments vs. the absolute value of effective temperature variation of rubber substrate during deposition. The properties of HNBR substrate and DLC film used for the estimate of segment size with Eq. (2) are: $E_s = 10.2$ MPa, $E_f = 150$ GPa; $\alpha_s = 180 \times 10^{-6} \text{ K}^{-1}$, $\alpha_f = 6 \times 10^{-6} \text{ K}^{-1}$; $t_s = 2$ mm, $t_f = 0.3$ μm ; $\nu_f = 0.13$.

emphasized that the inwards bent edge of the DLC film segments and close crack network are crucial for avoiding the impact between the surface asperities of the sliding counterpart and otherwise sharp edges of open cracks in a film, and thus preventing the formation of a large amount of wear debris that causes wear and high friction in practical applications [2]. Fig. 3c shows a close-up view of typical fracture cross-section of the DLC films that exhibit columnar structure and conform to the rough surface of the rubber substrate. The interfacial bonding between the DLC film segments and HNBR substrate is strong and can be well controlled by plasma cleaning of the rubber surface before coating deposition [5].

Fig. 4 plots the average size of DLC film segments (or equivalently the average spacing of crack network) vs. the absolute value of temperature variation ΔT . It is prominent that a larger value of ΔT yields smaller segments of a DLC film. Moreover, the size of DLC film segments can be turned in a large range, from hundreds micrometer to micrometers. It is understood that the size of the film segments or the crack spacing is determined by the thermal mismatch strain that depends on the ΔT exposed on rubber substrate during deposition. The crack spacing of DLC film on rubber substrates can be estimated as [4]

$$l \cong \frac{5.6}{(\alpha_s - \alpha_f)\Delta T} \sqrt{\frac{\Gamma_f t_f (1 - \nu_f)(E_s t_s + E_f t_f)}{E_f E_s t_s}} \quad (2)$$

where Γ_f is the fracture energy of DLC film, α , E , ν and t are the coefficient of thermal expansion, the modulus, Poisson's ratio and the thickness of DLC film (indicated by the subscript f) or rubber substrate (indicated with the subscript s), respectively. Consequently, the crack spacing is inversely proportional to ΔT , and also related to the fracture energy, effective modulus and thickness of DLC films. To verify the validity of Eq. (2), $\Gamma_f = 35 \text{ J m}^{-2}$ for DLC films [6,7] is used to estimate the average crack spacing (equal to the average size of film segments), and good agreement between experiment and theory is attained (see Fig. 4).

The density of crack network or segment size affects the flexibility and consequently the friction of DLC films coated HNBR rubber. Fig. 5a shows the tribological result of the DLC films of different segment sizes and also the CoF curve of uncoated HNBR as the reference that is ten times larger. All the CoF curves of DLC films coated HNBR start at an initially low value of 0.11–0.12 at the beginning of sliding and gradually increase to a steady state

Fig. 5. (a) Coefficient of friction of 300 nm thick DLC films coated HNBR with the average segment sizes indicated and uncoated HNBR. SEM micrographs showing the wear track of (b) DLC400-300V film (45 μm segment size) coated and (c) uncoated HNBR tested under the same condition: 1 N load, 10 cm/s sliding speed and against $\phi 6$ mm 100Cr6 steel ball.

of higher values. Clearly, the DLC films exhibit a monotropic relation between the size of film segments and the steady-state CoF such that the smaller the segments are, the lower the steady-state CoF is and also the shorter time to reach it. The initial low CoF reflects the “real” friction of DLC films themselves against the bearing steel ball. The increase of CoF in the onset of tribo-tests is related to the visco-elastic deformation of rubber substrates that

Fig. 6. SEM micrographs showing the evolution of wear morphology of the same area in a wear track on the DLC400-300V film (45 μm segment size) testing at 3 N normal load: (a) as deposited, (b) after sliding 1000 laps, (c) 2500 laps and (d) 10,000 laps. Arrows point to the polishing spots.

may be described with a “mattress” model, each element of the mattress is a simple arrangement of two springs and a dashpot known as ‘standard linear solid’ (SLS). The detailed simulation on the effect of the viscoelasticity of rubber substrates on the frictional behavior of DLC coated system will be published elsewhere [8].

The wear tracks of DLC film coated HNBR rubber are hardly visible in an overview of low magnification (see Fig. 5b), indicating superb protection to rubber substrates. It is in sharp contrast to the heavily damaged wear track of uncoated HNBR shown in Fig. 5c, where a layer distinguishable from the bulk rubber was formed on the wear track. This layer of rubbers was called “dead layer” with modified properties [9] and formed due to high flash temperatures during sliding and adhesive interactions between rubber and counterpart.

Intermittent SEM observation of the same area in a wear track may clearly monitor the evolution of wear process of DLC film coated HNBR rubber. The SEM micrographs in Fig. 6 reveal that DLC400-300V film of 45 μm average segment size showed a few new fracture cracks of micrometers size formed in the first 1000 laps of sliding under 3 N normal load, and thereafter only tiny polished spots occurred on the humps of convex segments till sliding for 10,000 revolutions. Most part of the surface area of the DLC film was intact after the tribo-test. In contrast, DLC films with larger segment sizes fractured more heavily during sliding against steel ball. In DLC400-400V film of 188 μm average segment size as shown in Fig. 7, newly formed long fracture cracks under 1 N normal load propagated through the entire segments in a brittle manner and

caused the formation of debris that scratched both the counterpart and DLC film itself, leading to higher friction as shown in Fig. 5a. Nevertheless, the fractured DLC film segments still adhered well to the rubber substrate, thanks to the high strength of interfacial adhesion.

To check the influence of viscoelastic deformation of rubber substrate, tribo-tests at different sliding velocities or with interruptions for different time periods from 150 s to 600 s were performed and the result is depicted in Fig. 8. After each interruption, the CoF dropped at the beginning of the successive tests and gradually increased again to reach the corresponding steady-state CoF, but the time needed to reach the steady-state CoF was proportional to the interruption period. This observation can be interpreted as such that the recovered amount of the viscoelastic deformation of rubber substrate in term of wear track depth is time related and the adhesive component of CoF is a function of contact area that depends on the depth of wear track. After a larger amount recovery of wear track depth, the CoF drops more because of smaller contact area and longer time is needed to reach the steady-state CoF. On the other hand, the sliding velocity of the counterpart ball in the ball-on-disk configuration determines the interval between each revolution and the rate of loading on individual locations in a wear track and thus affects the recovery of the viscoelastic deformation in the rubber substrate. Higher sliding velocity results in slightly larger CoF of the coated system, indicating more energy dissipated in the faster indentation process and delayed recovery of rubber deformation at higher frequencies of loading.

Fig. 7. SEM micrographs showing the evolution of wear morphology of the same area in a wear track on the DLC400–400V film (188 μm segment size) testing at 1 N normal load: (a) as deposited and (b) after sliding 10,000 laps. Open arrows indicate new fracture cracks and close arrows point to wear debris.

Fig. 8. The effect of sliding velocity and interruption time on the friction of DLC film coated HNBR.

4. Conclusions

Flexible DLC films of micrometer-scale segments have been deposited on HNBR rubber via self-segmentation. The size of film segments can be tuned by controlling the temperature variation of rubber substrate during deposition with the bias voltage applied for plasma CVD. The segmentation of DLC films is self-acting and fully controllable.

The dense crack network and the inward bent edge of film micro-segments contribute to the flexibility, ultra-low friction and wear resistance of DLC film coated rubber. This work provides a generic design rule for the deposition of flexible and low friction films on dynamic rubber seals and an approach to drastically reduce energy consumption in bearings and other lubrication systems.

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