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Microstructure and tribological performance of diamond-like carbon films deposited on hydrogenated rubber

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ABSTRACT

In this paper, the microstructure and tribological performance of diamond-like carbon (DLC) films prepared by plasma chemical vapor deposition on hydrogenated nitrile butadiene rubbers (HNBR) are studied. Different negative variations of temperature during film growth were selected by proper changes of the bias voltage. Raman measurements show a similar bonding regardless of the voltages used. A columnar growth and a tile-like microstructure of the DLC films were identified by scanning electron microscopy. Patch sizes can be correlated with the deposition conditions. The coefficient of friction (CoF) of DLC film coated HNBR was found to be much lower than that of the unprotected rubber, and more reduced for the DLC films with smaller patch sizes, which is explained by a better flexibility and conformity of the film during testing. In one of the samples, unexpected low CoF was observed, which was attributed to a modification of the mechanical properties of the rubber during the plasma treatment at high voltage. This issue was confirmed by X-ray photoelectron spectroscopy, which indicated a modification of the cross linking in the rubber.

1. Introduction

Diamond-like carbon (DLC) films are an optimal solution as protective coating for many applications, due to the combination of relatively high hardness, chemical inertness, low friction coefficient and low wear rate [1]. Their chemical composition, which is mainly constituted by C and H, suggests a good compatibility with rubber materials. Rubber seals incorporated in ball bearings are widely used in many technical fields, like aerospace or automotive industries [2], to prevent the leakage of lubricant and the entrance of dirt. However, under operation dynamic rubber seals suffer from severe wear and causes high friction, leading to an ultimate failure of the bearing. Therefore, a protective coating with optimal tribological performance is of much interest in the respects of energy saving and environment protection.

In our previous papers [3–5] we have demonstrated the possibility of tailoring the microstructure and flexibility of DLC films deposited with plasma chemical vapor deposition (p-CVD) on alkyl acrylate copolymer (ACM) rubber. That was achieved by defining the growth conditions in terms of thermal strain mismatch between DLC film and rubber substrate with changing bias voltage and treatment time. As a result, the temperature variation during film growth (ΔT) could be controlled, which determines the thermal stresses in the system and thus the final density of the crack network. It was also demonstrated that the bias voltage did not produce a major influence on the chemical bonding in the DLC films [3], and the differences in coefficient of friction (CoF) among the films were mainly related to the different microstructures. In addition, it was observed that the deposition in temperature drop (negative ΔT), namely rubber substrates under contraction, was a more effective process for reducing the patch size of DLC films and thus the CoF [4,5]. The work presented in this paper is aimed at studying the influence of different synthesis protocols with $\Delta T<0$ on the microstructure and tribological properties of DLC films deposited on hydrogenated nitrile butadiene rubber (HNBR).

2. Experimental details

DLC thin films were deposited on hydrogenated nitrile butadiene rubber (HNBR) by means of p-CVD in a Teer UDP/400 close field unbalanced magnetron sputtering rig, with all the magnetrons powered off. A pulsed DC (p-DC) power unit (Pinnacle Plus, Advanced Energy) was used as substrate bias source, operating at 250 kHz with a pulse-off-time of 500 ns and voltages between 300 and 600 V. Before deposition, the rubber substrates were cleaned by two subsequent washing procedures using a detergent solution and boiling water, in order to improve the film adhesion by removal of the dirt and the wax present in the rubber, respectively [4,6].

The deposition process was composed by two etching steps in Ar and Ar/H_2 mixtures, respectively, followed by the deposition in an

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Table 1
Synthesis conditions and average patch size of the samples under study.

Sample	Etching		Deposition		ΔT (°C)	Patch size (μm)
	Bias (V)	Time (min)	Bias (V)	Time (min)		
5V4	−500	35	−400	60	−25	83 ± 10
6V4	−600	35	−400	60	−62	80 ± 10
4V3	−400	40	−300	120	−19	49 ± 6
5V3	−500	35	−300	120	−49	27 ± 4
6V3	−600	35	−300	120	−89	19 ± 5

Ar/C_2H_2 environment. During these steps, the temperature of the rubber varied as a result of ion impingement. Therefore, depending on the bias voltage and treatment time, the temperature variations during the deposition can be controlled, and the microstructure of the film (i.e. the patch size) can be tailored due to the different thermal stresses during the growth [4,7]. In this paper, three different etching voltages were explored (400, 500 and 600 V), in combination with two deposition voltages (300 and 400 V). The overall etching time was set to 35 or 40 min, including a fixed etching treatment for 10 min under Ar/H_2. The deposition time was chosen to obtain a film thickness of about 300 nm. All the synthesis conditions together with the corresponding temperature variation (ΔT) during the deposition and the measured patch size of DLC films are summarized in Table 1. The samples are labeled with the voltages used for etching and deposition divided by 100 and separated by a 'V'. Further details about the deposition conditions are published elsewhere [3,4].

The microstructure was characterized by scanning electron microscopy (SEM), using a Philips XL30-FEG microscope operating at 3 kV acceleration voltage. The tribological performance was evaluated at room temperature on a CSM tribometer with a ball-on-disk configuration, operating at 35 ± 2% relative humidity controlled by a humidity regulator. The counterpart was a ∅6 mm commercial 100Cr6 steel ball. The tribotest conditions were 1 N normal load and 10,000 laps. The sliding speed and frequency are indicated in the figures.

Raman spectra were acquired to investigate the chemical bonding of these films by using a LabRAM Horiba Jobin Yvon spectrometer equipped with a CCD detector and a He–Ne laser (532 nm) at 0.2 or 2 mW in order to avoid damaging of the rubber substrate. All measurements were recorded for the wavelength range of 100–2000 cm^{-1} under the same conditions (10 s of integration time and 10 accumulations) using a 100× magnification objective and a 100 μm pinhole. X-ray photoelectron spectroscopy (XPS) was performed using a Surface Science SSX-100 ESCA instrument. The pressure in the measurement chamber was maintained below 10^{-7} Pa during data acquisition. The spectrometer is equipped with a monochromatic Al K_α X-ray source (1486.6 eV). The electron takeoff angle with respect to the surface normal was 37°, and the spot diameter of the analyzed area was 1000 μm. Sample charging was compensated by placing an Au grid 1 mm above the sample and by directing a flood gun onto the surface. No Ar^+ cleaning was performed on the samples. Deconvolution of the spectra involved Shirley background subtraction and fitting with a number of peaks consistent with the functional groups present on the surface.

3. Results and discussion

Fig. 1 shows the microstructure of the samples under study at two different magnifications. The images taken at a high magnification reveal a globular surface morphology, which reflects a columnar growth of DLC film [3]. In addition, a tile-like microstructure can be distinguished at a low magnification, in agreement with previous results [3,4,7]. The patch size can be estimated by averaging the length of straight lines connecting opposite sides of the patch, and the results are summarized in Table 1. For samples prepared at the same deposition voltage, a larger patch size is obtained at a lower etching voltage. In addition, for the same etching voltage, smaller patch sizes are obtained for samples deposited at a lower voltage. As a result, if one processing parameter is kept constant, a relationship can be found between ΔT and patch size in agreement with our previous observations [3].

Fig. 2a represents the Raman spectra of some samples prepared at different etching and deposition conditions together with the spectrum of the HNBR substrate recorded on the same condition. The spectra of the samples show a background which reproduces the spectrum of the uncovered HNBR, except for the appearance of the D and G peaks which is characteristic of the DLC film. Fig. 2b shows a magnified view of that region, after the subtraction of the spectrum of the HNBR rubber. All of the spectra look very similar, indicating that the bonding in the DLC film is not much affected by the bias voltage, as observed in the case of DLC deposited on ACM rubber [3].

The frictional behavior of two samples is depicted in Fig. 3. The values of CoF are much lower than the uncoated rubber, which reaches values around 1.3 [8]. This strong reduction of CoF is caused by a decreased adhesive interaction between the DLC film and the counterpart [3,8]. In addition, both curves show a similar behavior, starting at similar values of CoF around 0.12–0.13, and increasing afterwards to reach a steady state situation. For DLC-protected rubbers, the evolution of the CoF during a tribotest is determined by the rubber viscoelasticity [5,9–11]. In fact, it can be seen that the same type of film deposited on ACM shows a different frictional behavior, not

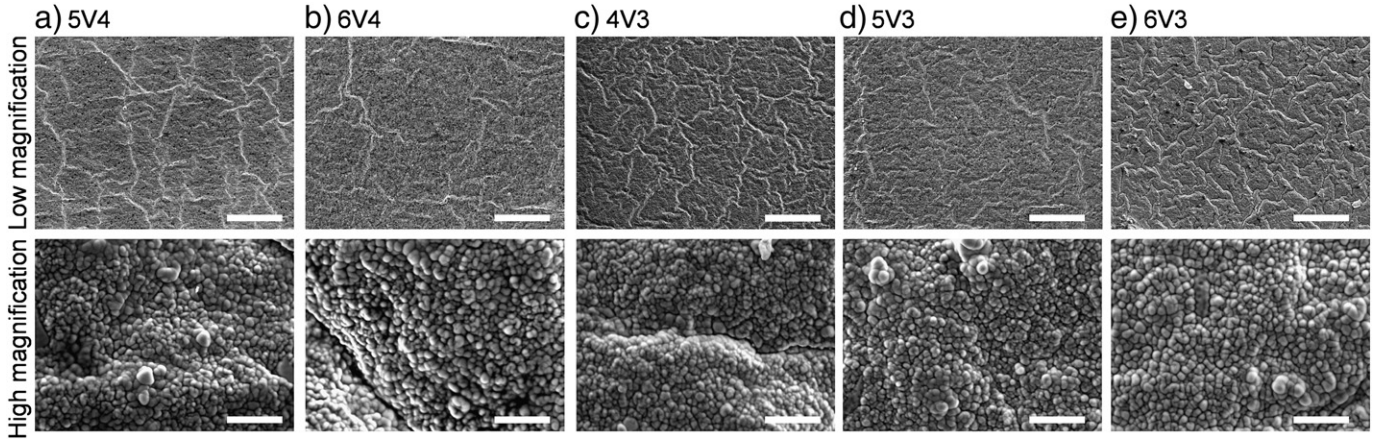

Fig. 1. SEM images of the samples under study at two different magnifications. Top: low magnification (scale bars 100 μm). Bottom: high magnification (scale bars 2 μm). a) 5V4, b) 6V4, c) 4V3, d) 5V3 and e) 6V3.