



High throughput deposition of hydrogenated amorphous carbon coatings on rubber with expanding thermal plasma



Y.T. Pei ^{a,*}, A.R. Eivani ^{a,1}, T. Zaharia ^b, A.V. Kazantzis ^a, M.C.M. van de Sanden ^b, J.Th.M. De Hosson ^a

^a Materials innovation institute M2i, Department of Applied Physics, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

^b Department of Applied Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

ARTICLE INFO

Article history:

Received 24 July 2013

Accepted in revised form 20 February 2014

Available online 28 February 2014

Keywords:

Hydrogenated amorphous carbon thin film

Expanding thermal plasma

Arc current

Microstructure

Tribology

ABSTRACT

Flexible hydrogenated amorphous carbon (a-C:H) thin film coated on rubbers has shown outstanding protection of rubber seals from friction and wear. This work concentrates on the potential advances of expanding thermal plasma (ETP) process for a high throughput deposition of a-C:H thin films in Ar/C₂H₂ plasma on nitrile butadiene rubber (NBR). The effect of the arc current on the microstructure, interfacial adhesion and tribological properties of the deposited a-C:H films on NBR is scrutinized. The temperature variation during the short ETP process is small and only yields sub-millimeter segmented a-C:H films, in consistence with a previously developed model. Increasing the arc current from 30 A to 75 A leads to smaller sizes of film patches (reduced from 940 μm to 125 μm), enhanced adhesion strength from 20.4 MPa to 91.8 MPa and higher hardness (from 5.5 GPa to 8.9 GPa) of the deposited a-C:H films on rubber. The tribological performance of the ETP a-C:H coated NBR is a compromise between the adhesion strength and hardness of the a-C:H films, with the coefficient of friction being reduced from about 1 (uncoated NBR rubber) to less than 0.25 of a-C:H film coated NBR.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Rubber seals are a major source of friction in lubrication systems and bearings where dynamic rubber seals are employed. In order to enhance the tribological performance of rubber seals, a protective coating with low friction, high wear resistance, good flexibility and strong adhesion to rubber surface is an attractive solution. For this purpose, diamond-like carbon (DLC) coatings have been deposited recently on rubber substrates and have demonstrated their effectiveness for the protection of dynamic rubber seals [1–7]. Much effort has been paid for improving the interfacial adhesion of DLC coatings on rubber, one of the most critical issues that determine the performance of the entire coated system [5]. DLC coatings have been deposited successfully with different plasma induced processes; nevertheless, all the processes are limited by the rather low production rates [1–7]. This problem may be solved by using a so-called expanding thermal plasma chemical vapor deposition (ETP-CVD) method developed for high throughput deposition of hard amorphous carbon coatings [8–10]. The ETP-CVD process has been used for fast deposition of hydrogenated amorphous carbon (a-C:H) coatings on metal substrates [11,12], but the method was not examined before for the deposition of a-C:H thin films on rubber.

The microstructure and nanostructure of DLC films influence the flexibility and thus the tribological performance of the DLC film coated

rubbers [1–7]. A new approach has been recently reported for depositing micro-segmented DLC films of superior flexibility on rubber [13]. The novelty of the approach is that the segmentation process of DLC films is self-adjusting throughout the growth with plasma-enhanced chemical vapor deposition (PECVD) and the size of the film segments separated by crack network can be well controlled at the micrometer scale. The friction of DLC film coated hydrogenated nitrile butadiene rubber is reduced proportionally with decreasing the size of DLC film segments [14]. In addition, variation in the hardness of DLC films can change the coefficient of friction (CoF) of the films and the wear resistance of the sliding system. Hardness can be adjusted over a wide range by tuning the sp³, sp² and sp¹ hybridized carbon and hydrogen content in the DLC film with changing the deposition conditions [15,16]. Among the deposition parameters of ETP-CVD in an Ar/C₂H₂ environment, arc current significantly affects the dissociation of acetylene molecules and hence the plasma chemistry in the substrate region [17]. As a result, changing the arc current can alter the hardness and tribological properties of ETP-CVD a-C:H films. Therefore, the effect of the arc current on the microstructure of the a-C:H films and tribological performance of the coated nitrile butadiene rubber (NBR) has been studied in depth.

The motivation of this work was to meet the requirement on a high throughput deposition of hard amorphous carbon film so as to reduce the production cost for industrial applications of a-C:H film coated rubbers, at a possible expense of slight performance degradation in comparison with the advanced flexible DLC films deposited with PECVD [13,14], which have passed a pilot production and machine tests.

* Corresponding author.

E-mail address: y.pei@rug.nl (Y.T. Pei).

¹ At the present with the School of Metallurgical and Materials Engineering, Iran University of Science and Technology, Tehran, Iran.

2. Experimental procedure

2 mm thick NBR rubber substrates of 45×45 mm size were first chemically cleaned for 15 min with 10% diluted ENDI detergent (Wieds Ecochem AG, Freudenberg, Germany) at 60 °C in an ultrasonic bath and then rinsed with dematerialized water. This procedure was repeated 5 times. Wax removal was carried out 3 times, each for 15 min, in the ultrasonic bath with hot (90–95 °C) demineralized water. The substrates were cooled in ambient air to room temperature before being loaded into the deposition chamber.

A sketch of the ETP-CVD apparatus is shown in Fig. 1. The reactor and experimental details have been described in detail elsewhere [18,19]. In short, the plasma was generated at sub-atmospheric pressures in flowing Ar gas (purity 99.999%, flow 20–50 sccs – standard cubic centimeters per second) at 3 symmetrically positioned cathode tips by a DC discharge, then transported through a narrow channel drilled in the center of 4 floating, mutually isolated, copper plates and finally expanded through a nozzle into the deposition chamber. Acetylene was admixed via an injection ring at the arc exit for a-C:H film deposition. The formed plasma mixture expanded into the cylindrical chamber with a diameter of 700 mm and was transported towards a substrate holder, situated 650 mm apart from the arc nozzle, where the rubber substrate was placed. Ar plasma cleaning of the NBR was first carried out for 10 min at 75 A arc current and 30 sccs Ar flow, in combination with -300 V r.f. (13.5 MHz) bias voltage applied on the substrates. Deposition of a-C:H films was performed at 50 sccs Ar flow and 4 sccs C_2H_2 right after the plasma cleaning, and no external substrate bias was applied. The substrate temperature was measured in-situ with a thermocouple inserted into the rubber substrate. The a-C:H films were deposited at different arc currents, from 30 A to 75 A, and thus named accordingly (i.e. film deposited at 30 A was named C30A). The deposition time was adjusted to yield the same film thickness of 800 nm and all other deposition parameters were kept constant. 8 to 10 samples of each film were produced for characterization and tribological tests. The detailed deposition parameters are listed in Table 1.

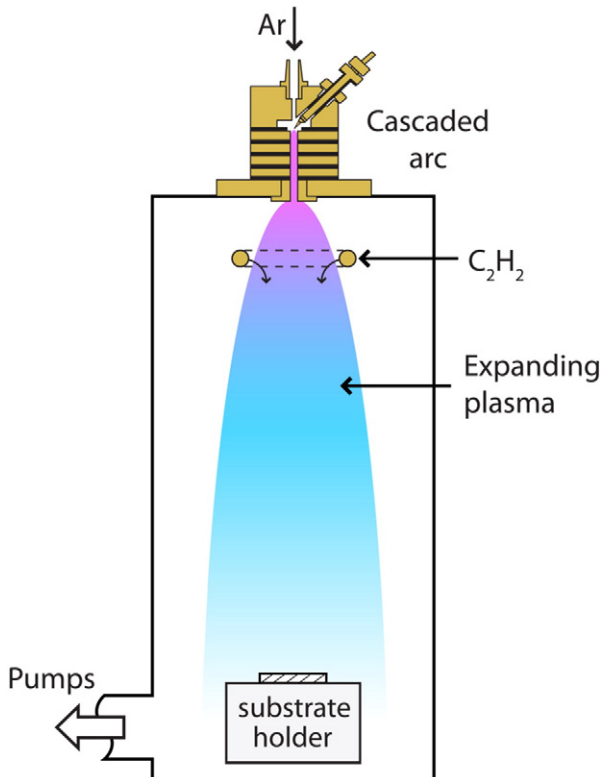


Fig. 1. Sketch of the ETP-CVD reactor.

Table 1

ETP-CVD deposition parameters and properties of the deposited a-C:H films on NBR.

	a-C:H film code			
	C30A	C45A	C60A	C75A
Arc current (A)	30	45	60	75
Ar flow rate (sccs)	50	50	50	50
C_2H_2 flow rate (sccs)	4	4	4	4
Pressure (Pa)	29	29	29	29
Start temp. (°C)	75	77	76	75
End temp. (°C)	77	79	79	79
ΔT (°C)	2	2	3	4
Deposition time (s)	240	210	180	150
Deposition rate (nm/s)	3.5	3.8	4.4	5.0
Film thickness (nm)	850 ± 50	800 ± 50	800 ± 30	750 ± 50
Patch size (μm)	940 ± 80	630 ± 30	350 ± 20	125 ± 15
Hardness (GPa)	5.5 ± 1.1	6.4 ± 1.1	7.8 ± 1.0	8.9 ± 0.9
Modulus (GPa)	39.6 ± 3.5	41.2 ± 3.9	55.3 ± 4.4	64.4 ± 3.5

The surface morphology and roughness of the a-C:H films on NBR were investigated using atomic force microscopy (AFM, Dimension III, Digital Instruments) and scanning electron microscope (SEM) (Philips XL-30 FEG environmental SEM). Raman spectra of the a-C:H films were obtained with a Horiba LabRAM HR Evolution system excited with a visible laser ($\lambda = 514$ nm). The tribological tests were performed at room temperature (20–23 °C) on a CSM tribometer with ball-on-disk configuration. The counterpart was a commercial $\phi 6$ mm 100Cr6 steel ball of hardness HRC 60–62. All the tests were carried out at a sliding velocity of 10 cm/s and normal load of 1 to 3 N, respectively, which corresponds to an initial contact pressure of 1.6 MPa to 2.3 MPa (assuming the modulus of NBR rubber 10 MPa as measured with indentation [3]). A constant humidity of $50 \pm 1\%$ was maintained in the testing chamber by adding either water vapor or dry air, depending on the ambient humidity, via a variable flow controller with feedback. The surface morphology and wear track of the a-C:H film coated rubber before and after the tribology tests were characterized by high resolution SEM. The wear scar of the counterpart balls was first cleaned with acetone in an ultrasonic bath to remove adherent wear debris and possible tribolayer, and thereafter investigated by confocal light microscopy (Nanofocus μSurf). By comparing the three dimensional profiles before and after tribo-test with a homemade code in Matlab, the wear volume was assessed with a margin of error of $\pm 3\%$.

The flexibility and adhesion strength of the a-C:H films were examined via in-situ tensile tests on coated specimens with gage section dimensions of $10 \times 3 \times 2$ mm³, with a homemade tensile stage installed in the SEM. The tensile stage was composed of two parallel crossheads, one fixed and the other moveable, with a maximum opening of 30 mm. The moveable crosshead was driven by a fine screw with a displacement resolution of 0.1 mm. At least three tensile tests were made for each coated sample, with in total more than 200 measurements of crack spacing per sample.

Nanoindentation with a calibrated MTS Nano Indenter XP employing a Berkovich indenter was used to measure the hardness (H) and Young's modulus (E) of the same a-C:H films deposited on silicon wafer to avoid the influence of compliant rubber substrate, which were merely considered as a relative measure of the property change with processing parameters. In order to have reliable statistics, 50 indentations in total were executed on three different areas of each coating sample. The maximum indentation depth for measuring H and E was fixed at one tenth of the coating thickness. The averaged H and E values over the depth range of 50–80 nm were taken as the corresponding hardness and modulus of the film.

3. Results and discussion

3.1. Microstructure of ETP-CVDed a-C:H film

The ETP-CVD process takes only 150–240 s to deposit 800 nm thick a-C:H films, and the deposition rate increases from 3.5 nm s^{-1}

Download English Version:

<https://daneshyari.com/en/article/8027918>

Download Persian Version:

<https://daneshyari.com/article/8027918>

[Daneshyari.com](https://daneshyari.com)