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Anode layer source plasma-assisted hybrid deposition and characterization of diamond-like carbon coatings deposited on flexible substrates

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ABSTRACT

Diamond-like carbon (DLC) coatings were deposited on nitrile butadiene rubber (NBR) substrates by physical vapor deposition (PVD)-like and chemical vapor deposition (CVD)-like methods. An anode layer source plasma generator was used for surface pre-treatment and deposition of DLC coatings by employing a hybrid method involving magnetron sputtering and plasma-enhanced chemical vapor deposition. The coatings were characterized by scanning electron microscopy, atomic-force microscopy, Raman spectroscopy, nanoindentation and contact-angle goniometer techniques. Due emphasis has been given to studying the tribological characteristics of the coatings under ambient conditions. Oxygen plasma pre-treatment of the NBR substrate, prior to the deposition, resulted in 18% improvement of the average coefficient of friction. Coatings deposited by the PVD-like method showed improved mechanical and tribological properties compared to those deposited by the CVD-like method. Explanations based on coating surface chemistry and microstructure are provided herein to support the relatively superior frictional performance and wear characteristics of the coatings deposited by the PVD-like method.

1. Introduction

Diamond-like carbon (DLC) coatings have attracted great attention in diverse engineering applications [1]. Ranging from cutting tools to razor blades, the application scope of DLC coatings is growing by leaps and bounds every day. Most of research and development involving DLC coatings have been focused on enhancing the mechanical properties of rigid substrates. Only in recent years, active research has been carried out on fabrication and characterization of DLC coatings on pliant substrates. In particular, elastomer-based pliant engineering components are believed to have had their mechanical performance greatly enhanced with the help of DLC coatings [2]. A comprehensive review of DLC coated elastomers can be found in Refs. [3, 4]. Some commonly used methods for the deposition of DLC coatings include magnetron sputtering [5], arc deposition [6,7] and plasma-enhanced chemical vapor deposition (PECVD) [8]. Utilization of anode layer source (ALS) plasma generators for PECVD of DLC coatings have attracted great interest due to increased coating production throughput, adhesion improvements [9] and increased nanohardness [10]. ALS is being commercially utilized for industrial-scale depositions of DLC coatings on float glasses [11]. Combining the positive attributes of magnetron sputtering and PECVD techniques are believed to have great advantages, such as adhesion improvements [12], over the individual deposition methods. *Lackner* et al. [13] deposited a-C:H coatings, with exceptional mechanical properties, by using a hybrid process involving simultaneous application of a radio-frequency (rf) PECVD and a rf magnetron sputtering on thermoplastic polyurethane substrates. *Jarratt* et al. [14] employed a similar hybrid method for fabricating DLC coatings with excellent wear resistance and adhesion to steel substrates. Such methods have also been quite helpful for depositing metal-doped DLC coatings [15,16]. In our previous paper [17], results obtained from ALS plasma-assisted hybrid deposition of DLC coatings on different elastomeric substrates were reported. However, the effect of variable deposition conditions on the coating properties is yet to be shown. In this report, we compare the properties of DLC coatings fabricated by using two different deposition conditions during the hybrid deposition method assisted by ALS plasma generator. Nitrile butadiene rubber (NBR) has been used as a model substrate for this study, as it has been inferred from our previous work [17] that DLC-coated NBR gave the best tribological performance compared to DLC-coated elastomers of other types reported in [17].

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Table 1
Parameters used for plasma pre-treatment of the substrate followed by DLC coating deposition.

Code	Description	Chamber pressure (× 10^{-5} Pa)	Gas flow (sccm)	Deposition rate (nm min^{-1})
T	Surface pre-treatment step	12	20 O_2 (ALS)	–
C1(T)	PVD-like DLC deposition step	114	42 Ar/8 C_2H_2 (Magnetron sputtering + PACVD)	2
C2(T)	CVD-like DLC deposition step	140	17 Ar/33 C_2H_2 (Magnetron sputtering + PACVD)	8

2. Experimental methods & characterizations

Plasma surface pre-treatment steps were performed using an anode layer source [*ALS 340 linear ion beam source*, *Veeco*, *USA*]. The same plasma source was used to generate Ar and C_2H_2 plasmas during the DLC deposition step consisting of simultaneous magnetron sputtering and PECVD. Before the plasma pre-treatment step, the substrates were subjected to a soap cleaning procedure reported elsewhere [12]. Experimental parameters of the plasma surface pre-treatment and the DLC deposition steps are described in Table 1. The gas flow ratios corresponding to DLC deposition step were chosen in such that one could compare two extreme cases of deposition methods representing physical vapor deposition (PVD)- and chemical vapor deposition (CVD)-like methods. The deposition time was fixed in such way that the coating thickness remained constant (~300 nm) for all depositions. Other deposition parameters are as follows: sputtering target power: 1.6 kW; target size: 3 in.; power used for anode layer source plasma generator: 1 kV; deposition pressure: 0.2 Pa; Further details about the deposition parameters can be found in our previous report [17]. Scanning electron microscopy of the as-deposited and the wear-tested surfaces was done by using a *Zeiss DSM 962* instrument. A *NanoSurf EasyScan 2* AFM (atomic force microscopy) equipment under tapping mode operation was used for surface roughness analysis (a scan size of 10 × 10 μm^2 was employed).

Surface-energy calculations were made from contact angle measurements using a *Kruess*, *DSA100* [18]. Nanoindentation studies were performed using a *Veeco Dimension 3100 - Hysitron Triboscope* equipment to measure hardness and maximum contact depth during indentation. The coatings were characterized using a Raman spectrometer (*Horiba Jobin-Yvon HR800*) equipped with an *Olympus BX41 optical microscope*. Wear tests were performed under ambient conditions at a load of 1 N using a *Bruker UMT-2 micro-tribometer* with the ball-on-disc configuration. The sliding distance and velocity employed were 1 km and 10 cm s^{-1}, respectively. The counterpart used was 100Cr6 stainless steel balls of 6 mm in a diameter (*grade-HRC 60/62*, *Kuegel Pompel*). An optical microscope (*stereo microscope*, *Olympus SZX12*) was used for imaging the wear scars left on the counterparts after each test.

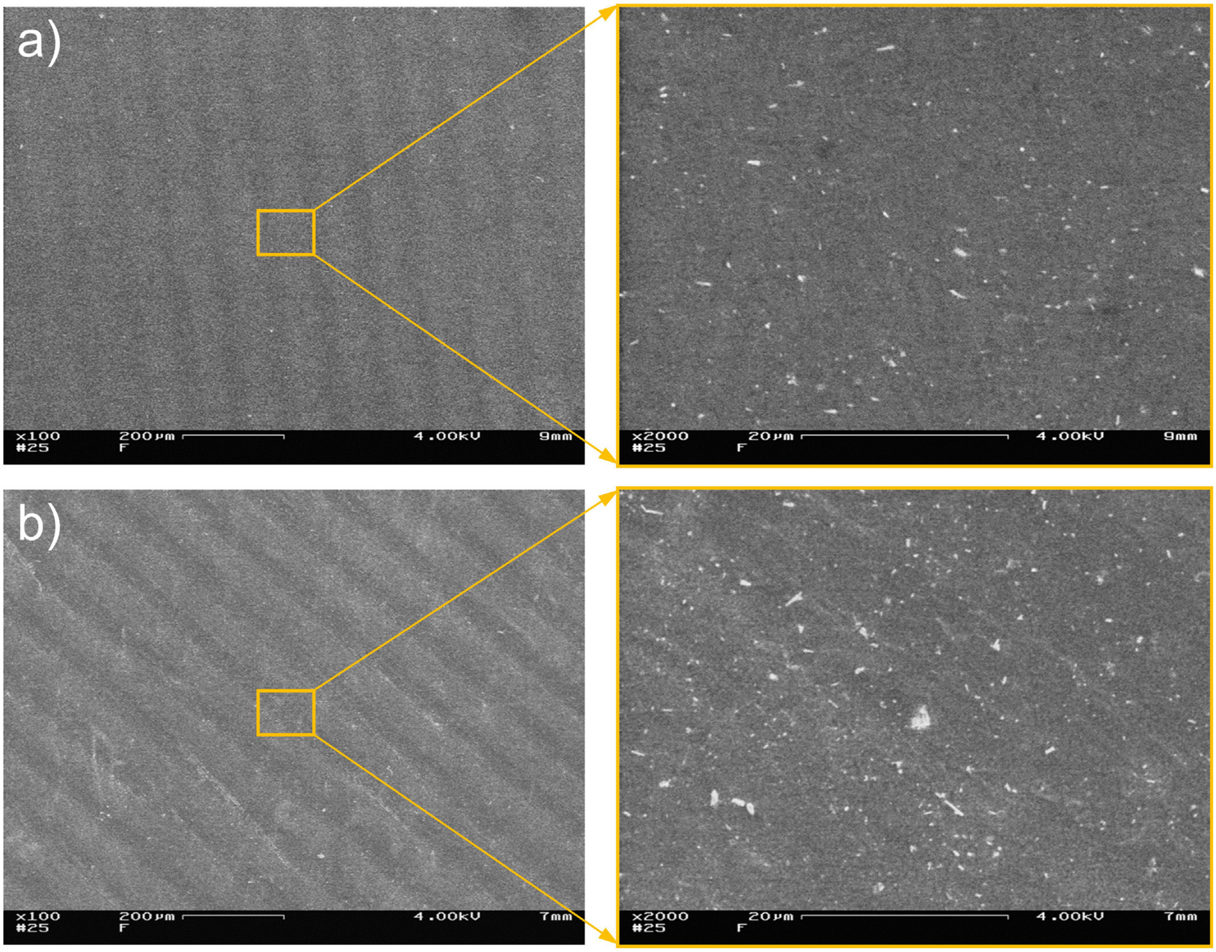

Fig. 1. SEM images of a) pristine-NBR (Mag. 100 ×) and b) plasma pre-treated NBR (Mag. 100 ×). High-magnification (2000 ×) images are shown to the right of the respective low-magnification (100 ×) images.