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Effect of the type of elastomeric substrate on the microstructural, surface and tribological characteristics of diamond-like carbon (DLC) coatings

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ABSTRACT

Diamond-like carbon (DLC) coatings are deposited by a hybrid process involving plasma-assisted chemical vapor deposition (PACVD) and pulsed direct-current (DC) magnetron sputtering on three different elastomer substrates, namely, nitrile butadiene rubber (NBR), fluoroelastomer (FKM) and thermoplastic polyurethane (TPU), under self-biased conditions. These DLC coatings and the corresponding elastomer substrates are characterized using confocal optical microscopy, scanning electron microscopy, atomic force microscopy and a contact angle goniometer. Tribological tests are performed using ball-on-disc configuration at a fixed load of 1 N under ambient conditions. Friction reduction after deposition of DLC coatings is highly effective in NBR (56.4%), followed by that in FKM (49.8%) and TPU (28.8%) substrates. Best wear resistance was shown by DLC-coated FKM, which was followed by DLC-coated NBR and TPU. Transfer film formation is believed to be the main tribological mechanism favoring better frictional properties of DLC-coated elastomers. This study elucidates the possible reasons for the differing frictional and wear performance of the three different DLC-coated elastomers under consideration.

1. Introduction

Tribology of polymers is very crucial in key applications of great economic and social importance like: automobile tires; seals used in oilfields [1], hand pumps in rural parts of Asian and African countries [2], turbines [3], polymeric bearing elements [4,5]. Tribological properties of elastomers need to be optimized according to the required application. For elastomer based sealing industry it is very important to reduce both friction and wear of the sealing components as far as possible by adopting appropriate strategies.

Common strategies used to achieve optimized tribological characteristics in elastomers include usage of appropriate: elastomers-filler compositions [6], appropriate physical design strategies [7], usage of appropriate lubricants [8], laser surface treatment [9], deposition of metallic coatings [10,11] and surface functionalization routes [12,13]. Each of these strategies has its own pros and cons. To quote a few examples of such: the application of lubricants may not be suitable in the initial and final stages of a tribo-test, where the boundary lubrication condition is predominant [14]; metal layers applied on elastomers do not seem to adhere well, though they appear to reduce friction to a certain extent [15]. One exciting and challenging strategy for elastomer-based industries is to make use of an external protective coating over the elastomers, which have already been positively tested on metallic substrates. Such a coating must be multifunctional, meaning that it should not only act as a friction reducing/wear resistant coating, but also protect against the degradation of the elastomer components by showing good chemical compatibility with the elastomer as well as the lubricant. The diamond-like carbon (DLC) coating is one candidate for such applications [16,17].

The first report on DLC-coated compliant elastomeric/polymeric substrates was published in the year 2004, where Nakahigashi et al. [18] reported their preliminary findings on flexible DLC-coated elastomers (like NBR) by the radio frequency-plasma assisted chemical vapor deposition (RF-PACVD) process. The coefficient of friction value was reportedly reduced to ~0.7 from ~1.6 after the application of DLC coating onto NBR. However, no indepth analysis of friction and wear characteristics of such coatings were presented in that report. Martinez et al. [19] also employed the aforementioned RF-PACVD process to deposit DLC coatings on NBR and HNBR elastomers. They found that the surface energy reduced upon applying a DLC coating to NBR, whereas the surface energy increased upon coating HNBR. This was attributed to an increase in oxygen-functional groups in DLC-coated HNBR. Lubwama et al. [20,21] have studied the adhesion, mechanical and tribological properties of DLC and Si-DLC coatings deposited on NBR substrates with/without an Si-C underlayer, using closed field unbalanced magnetron sputtering technique. A novel X-cut method is reported to study the coating adhesion and failure mechanisms. Incorporation of

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Si in DLC coatings and introduction of Si-C underlayers are reported to have a detrimental effect on the mechanical and tribological properties of the coatings. Pei et al. [22] have employed an expanding thermal plasma based deposition technique for high throughput deposition of a-C:H coatings on NBR substrates. The coefficient of friction was reportedly reduced to less than 0.25 from over 1, upon application of a DLC coating. They have investigated in detail the effect of an arc current on the tribological characteristics of DLC-coated NBR. Pei et al. [15,23] deposited W-DLC on FKM, ACM and HNBR based elastomeric sealing materials by using unbalanced reactive magnetron sputtering, and studied their microstructural and tribological characteristics. Synergic effect involving good coating adhesion and flexibility attributed to the patch-like microstructures are reported as the attributes of high wear resistance and good quality W-DLC coated elastomeric seals. However, the friction reduction mechanisms are not reported in-detail. Masami et al. [24] reported the low temperature (30 K) deposition of Si-DLC coatings on FKM elastomers with the help of a bipolar pulsed plasma based ion implantation (PBII) system. Si-DLC coatings deposited by that technique show very high wear resistance and a low friction coefficient (0.2 to 0.25). Lackner et al. [25] deposited a-C:H coatings on TPU substrates using a hybrid process involving RF-PACVD and RF-Magnetron sputtering. Those coatings reportedly showed exceptional mechanical properties. Two major gaps are found in the literature for DLC coated elastomers: a) no detailed correlation is established between the surface characteristics and tribological properties of DLC-coated elastomers; b) the effect of the substrate type on the tribological properties of DLC-coated elastomers is not explored in detail. We have attempted to fill these gaps in this article. Three elastomeric substrates, namely, NBR, FKM and TPU, were used in this study to understand how different elastomeric substrates affect the surface and tribological characteristics of DLC coatings.

2. Experimental methods & characterisations

The three types of injection molded elastomeric substrates, viz., NBR, FKM and TPU, were cut into the following sizes: 20 × 20 mm, and 35 × 35 mm and were subjected to standard cleaning procedures [26]. Cut elastomeric substrates were cleaned first in a soap solution filled in an ultrasonic bath for 10 min, followed by cleaning in hot distilled water (80 °C) filled in an ultrasonic bath for 10 min. This hot water cleaning procedure was repeated three times, after which the samples were rinsed in distilled water and dried in a hot air oven for 15 min at 100 °C. After this step, the substrates were stored overnight in a desiccator and subsequently packaged for plasma pre-treatment and DLC deposition. This cleaning procedure was believed to be a very crucial one, as the actual microstructures of the elastomers seemed to be exposed only after this step due to de-waxing process that happens during this cleaning process [26].

Plasma pre-treatments were performed using an anode layer source (ALS) [ALS 340 linear ion beam source, Veeco, USA] at 1 kV DC acceleration voltage at 20 sccm O_2 gas flow, resulting in pressures in the low 10^{-4} mbar regime [27]. This was followed by DLC coating deposition using a hybrid technique involving pulsed DC magnetron sputtering and the PACVD method [28]. A graphite target (electrographite, 99.5% purity, Schunk, Bad Goisern, Austria) was used as a sputtering source for pulsed DC sputtering at 80 kHz frequency and 1600 W sputtering power. 17 sccm Ar and 33 sccm C_2H_2 were used as gas flows for the sputtering (reaching 2×10^{-3} mbar pressure). ALS was used for the generation of Ar and C_2H_2 plasmas. Substrates were fixed on the substrate holder at 12 cm distance to the sputtering target under self-biased condition (due to its highly insulating nature), with the substrate holder being grounded. One of the greatest advantages of pulsed DC sputtering over other types of sputtering is that the particle emission from the target is not favored, as arcing effects are avoided by pulsing [29]. The plasma pre-treatment and DLC deposition conditions employed are reported in Table 1.

Table 1
Main process parameters used for plasma pre-treatment (T) and coating deposition (D) [30].

Code	Gas flow
T	20 sccm O_2 (ALS)
D	17 sccm Ar + 33 sccm C_2H_2 (Magnetron sputtering + PACVD using ALS)

The code T refers to the parameters used for plasma pre-treatment using ALS O_2 plasma, and the code D refers to DLC deposition applied on the plasma pre-treated elastomeric substrates. Process parameters were chosen in such a way that the coating thickness is more or less 300 nm in all the coatings. An optical microscope (*Stereo Microscope*, *Olympus SZX12*) was used to analyse wear scars on the stainless steel counterpart balls used for tribo-testing. A confocal microscope, based on the focus variation technology [31] (*Alicona*, *InfiniteFocus*), was used to characterize wear tracks. Scanning electron microscopic (SEM) analysis was performed using a *Zeiss DSM 962* instrument with a Si (Li) detector, and a LaB_6 cathode to characterize the coating microstructures and wear tracks. Only TPU substrate based samples were sputtered with gold of 5 nm thickness, as the electron charging effect was found to be severe in TPU based samples. Coating surface roughness was performed using a *NanoSurf EasyScan 2* atomic force microscope (AFM). An aluminum-coated silicon-based commercial cantilever (Model: *Tap-190Al-G*) with a tip radius less than 10 nm was used. Topographic images from three different regions of a given sample were recorded of the size: 10 μm × 10 μm. Each of those three images was post processed using *Gwyddion v2.37* software. Average roughness was calculated by taking the average of area roughness measured three different regions in a sample. Liquid contact angle measurements were made using an contact angle goniometer (Model-*Kruess*, *DSA100*). The test procedure adopted was according to the ISO standards [32]. Two liquids, distilled water and Diiodomethane, were used for surface energy determination. Drops of 1 μl volume were used during every measurement. For statistics, 3–5 sets of contact angle readings were taken into account for calculations. Tribological tests were performed using ball-on-disc test configuration using a micro tribometer (*UMT-2*, *Bruker*). Tribological test parameters were: wear track diameter-10 mm; number of cycles/laps-10,000; counterpart material - 100Cr6 stainless steel balls of 6 mm diameter (grade-*HRC 60/62*, *Kugel Pompel*); sliding velocity-10 cm sec^{-1}; test load-1 N; frequency of data acquisition - 60 Hz and were under ambient conditions.

3. Results

Three different types of engineering elastomers, NBR, FKM and TPU, coated using the same deposition condition D shown in Table 1, are discussed in this section. The term ‘coated elastomers/surfaces’, refers to the elastomers subjected to the O_2 plasma pre-treatment step (T) followed by the DLC deposition step (D). Furthermore, the term ‘uncoated elastomers/surfaces’, refers to the elastomers subjected only to O_2 plasma pre-treatment step without any DLC deposition step.

3.1. Scanning electron microscopic characterisation

In uncoated-NBR (Fig. 1a), stripe-like structures and particle-like structures are noticeable in low and high magnification images, respectively. The presence of stripe-like structures is attributed to the injection molding die used in the NBR manufacturing process. The particle-like structures are attributed to the de-waxing of the NBR elastomer during the substrate cleaning procedure [26] described in the previous sections. In the coated-NBR (Fig. 1b), the DLC coating is seen with patch-like structures. These structures are separated by a bridge-like sandwich layer, as seen in the high magnification image of Fig. 1b.

In contrast to the large-patch-like microstructure observed in coated-NBR, coated-FKM (Fig. 2b) shows fine patches, rough and grainy