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Combination of laser surface texturing and DLC coating on PEEK for enhanced tribological properties

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ABSTRACT

Poly-ether-ether-ketone (PEEK) is a thermoplastic polymer marked by high mechanical properties and chemical inertia. PEEK is also a well-known biomaterial which has been subjected to intensive research over the last decades. In particular, it has recently been shown that laser surface texturing as well as diamond-like carbon (DLC) film deposition was able to reduce PEEK wear in tribological testing.

This study focuses on evaluating the mechanical and tribological performance of PEEK surfaces modified via laser surface texturing (LST) combined with DLC coating. An ultrashort-pulse laser was used in order to pattern a hexagonal array of 33 µm in diameter dimples onto the PEEK surface. The depth of dimples was varying (2, 12 and 21 µm) as well as the dimple density (10, 30 and 48%). Subsequently, a 2-µm thick DLC film was deposited on the textured PEEK surface.

It was shown that LST did not significantly affect the DLC/PEEK adhesion in pull-off testing, however, deep dimples and high dimple densities led to a large deformation of the substrate and caused the film to be more susceptible to cracking in scratch testing. The DLC-coated LST PEEK surfaces were rubbed against an alumina ball in dry conditions, water and bovine calf serum solutions. DLC-coated PEEK with shallow dimples and a low dimple density enabled to significantly, reduce wear and friction in distilled water and reduce wear in bovine calf serum compared with smooth DLC-coated PEEK. Smooth and LST DLC films exhibited a great stability in terms of microstructure and chemistry in all tested media.

1. Introduction

Poly-ether-ether-ketone (PEEK) is a high-performance thermoplastic polymer used in many industrial applications for its remarkable mechanical properties, chemical inertia and high glass transition temperature. PEEK is also known for its biocompatibility and increasingly used as a biomaterial for orthopedic implants [1].

Over the last decades, surface engineering has been trying to provide new surface functionalities to biomaterials, such as a better osteointegration or lessen inflammatory responses [2–4]. Many attempts aiming at reducing wear of biomaterials have been made for orthopedic implants because wear debris generation was identified as the main long-term failure mode of implants [5].

In particular, coating a surface with a hard film is one of the common strategy in order to reduce wear. Diamond-like carbon coatings were proven to be effective in reducing wear of biomaterials in in-vitro testing [6,7]. In a previous work, we showed that coating PEEK with a very soft hydrogenated amorphous carbon film enabled to significantly reduce wear [8].

Another possible strategy enabling to reduce wear is to give a specific topography to the rubbing surfaces. Typically, dimples or grooves are patterned onto the surface. Shallow dimples or grooves, typically a few hundred nanometers to a few microns deep, are supposed to enhance lubrication and act as lubricant reservoirs in boundary lubrication conditions. In the case of deeper dimples or grooves, typically a few micrometers to tens of micrometers deep, the dimples or grooves are supposed to trap wear debris and thus reduce abrasive wear. Surface patterning can be achieved via various processes such as lithography, knurling or laser ablation (also called laser surface texturing) [9]. In particular, Hammouti et al. [10] showed that laser surface texturing (LST) enabled to reduce wear in a PEEK/PEEK contact.

Combining both hard coating deposition and laser surface texturing on hard substrates showed promising results in terms of wear and/or friction reduction depending on the shape and geometric characteristics

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of the final surface [11–14]. In particular, Petterson et al. [12] showed that the groove patterns had to be perpendicular to the sliding direction or small square patterns (compared with the contact size) were necessary in order to avoid delamination of the film. In other words, they showed that the sliding direction as well as a large number of patterns in the contact area was crucial in order to achieve wear and/or friction reduction. When combining hard coating deposition and laser surface texturing, two approaches must be considered. As described by Dumitru [15], laser surface texturing of thin films can be performed before film deposition or after film deposition. The former is called indirect laser processing and the latter is called direct laser processing.

In the presented work, we investigate the mechanical and tribological behaviors of an indirectly laser processed DLC coating deposited on PEEK, that is to say, a DLC coating which was deposited on a laser surface textured (LST) PEEK substrate. More precisely, the influence of geometric parameters on the mechanical properties of the DLC-coated LST PEEK and its tribological behavior in various media is studied.

2. Materials and methods

2.1. Sample preparation

2.1.1. PEEK material

The PEEK polymer used in this work was a semi-crystalline natural (i.e., non-reinforced) PEEK (Victrex PEEK 450G). The PEEK test samples were machined from an injection-molded bar of 25.4 mm in diameter and were either 10 mm in diameter or 25.4 mm in diameter. The 10 mm in diameter samples were used for tribological testing whereas the 25.4 mm in diameter samples were used for all the other characterizations.

Different polishing cloths soaked with diamond pastes or alumina suspension were used in order to obtain a mirror-finish PEEK surface. Before laser surface texturing, the PEEK samples were, subsequently, ultrasonically cleaned in ethanol and distilled water for 10 min and then dried using a nitrogen blast.

2.1.2. Texturing/geometric patterns

In this work, indirect laser processing of thin tribological films, i.e. laser processing before coating deposition, was chosen in order to prevent collateral film damage due to laser exposure [15].

The PEEK surface was patterned by a hexagonal array of 30 μm in diameter dimples. The dimple depth as well as the dimple density, i.e. surface area density covered with dimples, were varying. Fig. 1 summarizes the various dimple depths d and dimple densities A and also shows the PEEK samples after laser surface texturing and before film deposition. Laser surface texturing was performed with the help of an ultrashort-pulse laser processing (Ultrafast Surface Design Platform, MANUTECH-USD). The ultrashort pulses were 400 fs long. The laser was a high power ultrafast fiber laser system (Tangerine, Amplitude Systemes) with a wavelength of 1030 nm and a circular beam shape. Assuming a laser power of 220 mW, a laser repetition rate of 50 kHz and a Gaussian beam profile, the peak fluence was 1.2 J cm^{-2}. The laser fluence was kept constant so that the dimple depth was adjusted by the number of pulses.

2.1.3. Post-texturing polishing

Laser processing of the substrate prior film deposition usually requires a soft post-texturing polishing of the substrate [15]. Laser ablation generated bulges with heights varying between a few hundred nanometers to 1 μm around the dimples. Therefore, a soft post-texturing polishing was performed in order to remove these bulges before film deposition. This soft post-texturing polishing did enable to remove the bulges, but also caused wear on the edges of the dimples and resulted in a slight increase in dimple diameter. The dimple diameter increased from 30 μm to 33 μm.

2.1.4. DLC deposition

Prior to film deposition, the laser surface textured and smooth PEEK samples were ultrasonically cleaned in a polymer-dedicated detergent (Galvarep200, NGL Cleaning) for 3 min and, subsequently, rinsed in 6 water baths and an isopropanol bath before being dried with a dry air blast. Before film deposition, an oxygen plasma treatment was performed in order to create dangling bonds as well as C—O bonds at the PEEK surface. A hydrogenated amorphous carbon film was deposited by plasma enhanced chemical vapor deposition (PECVD) from a gas mixture of argon and acetylene. A 2-μm thick layer was obtained after 120 min of deposition.

The C1s XPS spectrum of the DLC film was published in [8] and exhibited both sp^2 C=C and sp^3 C—C main contributions as well as a residual C—O contribution. According to Kaciulis [16], the deconvolution of both C1s C=C and C—C lines by peak fitting is not suitable for the reliable quantification of carbon hybridizations, due to insufficient energy resolution considering the proximity of the both contributions. In contrast, the determination of the width of the C_{KLL} signal obtained from Auger Electron Spectroscopy (AES), called "D parameter", is suitable for the quantification of the carbon hybridizations. Fig. 2 exhibits the derivative of the C_{KLL} AES spectrum of the DLC film, from which was deduced a D parameter of 16.3 eV. This value of D parameter corresponds to a Csp^2 content of 34.2%, according to the linear dependence of D versus Csp^2 published by Kaciulis [16].

The hydrogen content of the DLC film was not directly measured, but it was certainly ranging between 40 and 50 at.%. Indeed, a DLC film deposited in similar conditions, except with an additional bias voltage of − 50 V, contained 36 at.% of hydrogen [17]. Since the present DLC film was deposited without biasing and that, in such DLC films, it is known that ion bombardment of the growing film results in "dehydrogenation" [18] (i.e. hydrogen removal), its hydrogen content was probably higher than 36 at.%. Additionally, given that the hydrocarbon precursor contains 50 at.% of hydrogen, the hydrogen content of the DLC film cannot be higher than this value.

Green light interferometry (Brucker Contour GT-K1, Brucker Corporation) was used in order to assess the final surface topographies of the DLC-coated laser surface textured (LST) PEEK. A 50 × Mirau objective combined with a 0.5 × lens was used in vertical shifting interferometry mode.

2.2. Mechanical characterizations

2.2.1. Pull off tests

In order to study the effect of laser surface texturing on the adhesion between PEEK and the diamond-like carbon film, a pull-off adhesion tester (Positest AT-M, DeFelsko Corporation) was used. 10 mm in diameter aluminum dollies were fixed to the DLC-coated PEEK surfaces using a bi-component epoxy glue, which was cured for 120 min at 80 °C. The normal pull-off force was monitored throughout the test so that the maximum pull-off force would be measured. The pull-off tests were duplicated for all DLC-coated LST and smooth PEEK.

Scanning electron microscopy (Mira3, Tescan) and optical microscopy were carried out in order to observe the fracture surfaces. Some of fracture surfaces were further investigated by performing FIB cross-sections (Dual Beam HELIOS 600i, FEI).

2.2.2. Scratch tests

In order to assess the effect of laser surface texturing on the mechanical strength of the DLC film and the DLC-PEEK interface, scratch testing (CSM scratch tester, CSM Instruments) was performed in increasing load mode (ILM) using a 200 μm Rockwell C tip. The normal load was linearly increased from 1 to 15 N with a tip speed of 10 mm/min and a loading speed of 50 N/min. 2.8 mm long scratches were performed. The critical load L_c was determined by optical microscopic observation. The scratch tests were triplicated for all DLC-coated LST and smooth PEEK.