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Parylene coatings on stainless steel 316L surface for medical applications — Mechanical and protective properties

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ABSTRACT

The mechanical and protective properties of parylene N and C coatings (2–20 μm) on stainless steel 316L implant materials were investigated. The coatings were characterized by scanning electron and confocal microscopes, microindentation and scratch tests, whereas their protective properties were evaluated in terms of quenching metal ion release from stainless steel to simulated body fluid (Hanks solution). The obtained results revealed that for parylene C coatings, the critical load for initial cracks is 3–5 times higher and the total metal ions release is reduced 3 times more efficiently compared to parylene N. It was thus concluded that parylene C exhibits superior mechanical and protective properties for application as a micrometer coating material for stainless steel implants.

1. Introduction

Stainless steel (SS) is one of the most frequently used implant materials for internal fixation because of its cost-effective mechanical strength and the possibility of adjusting the shape of the implant to create a custom fit. Examples of SS applications include fracture fixation plates, screws, femoral stems, nails and pins, supports for heart valves and many others [1]. However, SS does have some significant disadvantages; the most common is surface corrosion. Upon prolonged contact with human tissue (elevated temperature and saline conditions) surface corrosion takes place and leads to the release of harmful products [2]. This in turn may result in allergy and dangerous diseases [3]. The ions released from SS surfaces are mostly of iron, nickel and chromium. Therefore appropriate engineering of the metal implant surface is of critical importance when attempting to limit the metal ions release process. Some general strategies concerning conventional surface preparations (e.g. polishing, passivation) and the application of coatings (e.g. glass, ceramic or polymer layer) for surface protection against metal ion release are discussed in [4,5].

One of the polymer family used for coatings today is poly-para-xylylene, known as parylene N, C and D. However, for application in medical devices only parylene N and C types (see Fig. 1) are currently approved by Biological Evaluation of Medical Devices as ISO 10993 (USP class VI polymer) [6,7]. These two polymers, easily vacuum-deposited, exhibit excellent mechanical properties (Table 1), biocompatibility, forming continuous, thin and inert films on metallic substrates [8]. Previous long term exposure tests in simulated body fluid (Hanks solution) revealed that a parylene N layer can be successfully used for corrosion protection of the SS surface [9]. Nevertheless, in more sever conditions (addition of H_2O_2) of simulating organism inflammatory response, due to formation of $OH^{\cdot}$ radicals, degradation of parylene N coatings were observed. After 7 days of tests the cracks of 100 nm width appeared in polymer as revealed by SEM observations [9]. Parylene C, as material with higher thermal stability and chemical/moisture resistance than parylene N, can be more suitable for anticorrosion applications [10]. However, both these polymers, parylene N and C, do not exhibit strong adhesion to inorganic surfaces to promote adhesion, pre-treatment with the silane A174 is recommended for pretreatment of steel surfaces [11].

Investigations on polymer coatings used for medical devices aim at increasing the corrosion resistance while decreasing the release of metal ions into the body. Additionally, these coatings form a support for bioactive substances, generating a suitable interface between the implant and the adjacent part of the organism [12]. Another important characteristic of the coating involves its mechanical properties, such as hardness, elasticity and friction [13]. These features are of key

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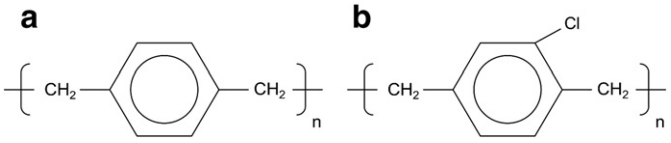

Fig. 1. Parylene N and parylene C polymers.

importance since during the surgical procedure and then daily usage mechanical damage of the implant surface (ex. scratches made by tools) can result in exposure of the underlying metal surface to aggressive body fluids [14]. The most important mechanical properties of the coatings are determined with the use of indentation and scratch tests [15,16]. It is thus important, when designing the surface of metal implants, that the coating, besides its biocompatibility, exhibits not only appropriate protective functionality, but also optimized mechanical properties. In this study, we focused on the investigations of the mechanical properties of polymer coatings and metal ion release from SS 316L to the simulated body fluid of Hanks solution. Two kinds of micrometer polymer coatings, parylene N and C, prepared by chemical vapor deposition (CVD) on the silanized stainless steel surface were evaluated.

2. Experimental

2.1. Materials

Samples of SS 316L grade (Fe — base, C — 0.03, Cr — 16.82, Ni — 10.02, Mn — 1.26, Mo — 2.07, Si — 0.46, N — 0.04, P — 0.02 wt.%) [17], cold rolled using highly polished rolls and bright annealed (BA) surface finishing, were supplied by Swerea KIMAB AB. The composition of the investigated SS material was verified by X-ray fluorescence (XRF) spectrometry revealing a discrepancy between several samples of less than 2%. Prior to analysis, samples were cut in square coupons of 30×30 mm^2 with a thickness of 0.8 mm. The surfaces of the samples were cleaned and pickled, passivated and coated by the following procedure. Firstly, the metal surface was covered by a monolayer of silane A174, using a dipping method (solution: 0.5 vol.% of methacryloxypropyltrimetoxy-silane in 50% water/50% iso-propanol, immersion time: 30 min, drying process: high pressure argon at 65 °C for 30 min). In the second stage, the coatings with parylene N or parylene C were applied via chemical vapor deposition (CVD) by Para Tech Coating Scandinavia AB. Dimer-di-p-xylylene was used as a precursor, decomposition to monomeric form was at 650 °C, spontaneous deposition and polymerization was at room temperature. The thickness of parylenes coatings was controlled by the deposition time. For the investigations, coating thicknesses of 2, 8 and 20 μm were applied. Such a covering procedure leads to the fabrication of thickness-defined and uniform surface protective coatings.

The samples were characterized by scanning electron (FEI E-SEM XL30) and laser confocal (Olympus LEXT OLS3100, laser line 408 nm LD Laser/Class 2) microscopes. The low accelerating voltage (0.8 kV) applied in SEM observations was used to avoid the destruction of the polymer coating and eliminate a need of application of additional conducting film. In Fig. 2, the examples of uncoated and parylene coated SS 316L surface are shown. As can be inferred from the SEM images, the deposition of both parylene N and C provide with smooth and uniform surfaces. This is in line with the confocal microscopic observations, where the cross section of the sandwich-like structure coatings can be seen (Fig. 3).

Table 1
Typical properties of parylene N and C polymer coatings [7].

Typical properties	Parylene	
	N	C
Tensile strength [MPa]	45	69
Field strength [MPa]	2.4	3.2
Elongation at break [%]	40	200
Density [g/cm^3]	1.110	1.289
Dielectric strength, short time [V/m]	7000	6800
Surface resistivity, 23 °C, 50% RH [Ω]	1×10^{15}	1×10^{15}
Dielectric constant: 60 Hz	2.65	3.15
Melting temperature [°C]	410	210
Moisture vapor transmission [g/m²/24 h]	1.50	0.14

2.2. Methods

2.2.1. Test of mechanical properties

Microhardness and Young modulus of the prepared coatings were measured using instrumented indentation method with the use of MCT-CSM Instruments apparatus. For the measurements Vickers geometry diamond and load of 10 and 20 mN were used. Loading and unloading rates were 20 and 40 mN/min, respectively. Maximum penetration depths during indentation were 1300 and 1800 nm for the load of 10 and 20 mN, respectively. The indentation data were analyzed by the Oliver and Pharr method [18], described in detail elsewhere [19]. Since the parylene polymers are hydrophobic and hardly influenced by the environmental conditions the mechanical tests were performed in ambient conditions (temperature of 22 ± 1 °C, humidity of 42 ± 3%) lead to representative and reproducible results. The six independent indentations were done for each sample.

Hardness of the coating (H) was calculated as a ratio of maximum load (F_{max}) and projected area (A_c) following the formula:

$$H = \frac{F_{max}}{A_c} \tag{1}$$

The contact area was calibrated with the use of a standard silicon substrate.

Reduced elastic modulus (E_z) of the coating can be determined according to the formula:

$$E_z = \frac{\sqrt{\pi}}{2}\frac{S}{\sqrt{A_c}} \tag{2}$$

where: S is a contact stiffness and can be obtained from the slope of the linear part of the unloading curve.

Taking into account the diamond indenter properties ($E_i = 1140$ GPa, $\nu_i = 0.07$) the elastic modulus of the polymer (E_m) was analyzed according to the formula:

$$\frac{1}{E_z} = \frac{1-\nu_i^2}{E_i} + \frac{1-\nu_m^2}{E_m} \tag{3}$$

For the investigated polymer coatings Poisson ratio $\nu_m = 0.4$ was assumed.

Scratch resistance of the investigated coatings was evaluated by the scratch technique [20] using a Rockwell C spherical diamond stylus with cone apex angle of 120° and tip radius of 200 μm. A typical scratch test consisted of three parts: a "prescan" when surface profile is measured under 10 mN load, a main part when load rises linearly from 10 mN to 10 N within the distance of 10 mm and a "postscan" when a profile of scratch track is measured again under a low load of 10 mN. Steady speed of 10 mm/min was used.

A coefficient of friction, friction force and applied load, indentation depth and acoustic emission were recorded. After the tests, scratch tracks were observed by optical microscopy with magnifications of 200× and 500×. As a result of such observations critical loads that caused cohesive cracks (L_{C1}) and coatings removal (L_{C2}) were obtained. For each sample, the average values of three independent measurements were determined.

2.2.2. Test of metal ions release

In vitro metals release investigations were performed in Hanks solution of Aldrich analytical grade (NaCl — 0.8 g; $CaCl_2$ — 0.02 g;