Structural and mechanical properties of Ta-based coatings deposited on polymers for biomedical applications

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Abstract. The polypropylene meshes currently used for hernioplasty induce severe chronic inflammatory reactions over a long-term period of use. These processes lead to scarring and have a negative effect on the connective tissue and the abdominal walls. It is well-known that the biocompatibility of polymer surfaces might be improved by surface modification. We report on the structure and composition of nanostructured Ta, Ta₂O₃, and TaON coatings deposited on polypropylene in correlation with their mechanical properties. The elemental distribution and chemical composition of the coatings were analyzed by energy dispersive X-ray spectroscopy. The coatings cross-sectional structure and morphology were observed by electron scanning microscopy. Mechanical tests were performed of the polypropylene and of the samples with Ta-based coatings to evaluate the Vickers hardness and the elastic modulus. The coated samples exhibited higher nano-hardness and elasticity values, significantly exceeding the values of untreated polypropylene samples. The Ta-based coatings deposited by magnetron sputtering improve the mechanical characteristics and biocompatibility of the polypropylene materials in view of, e.g., hernia repair.

1. Introduction
Ta-based materials and coatings are excellent endoprosthetic biomaterials for use in trauma and cardio-vascular surgery. Tantalum has also been selected as an alternative to other commonly used metallic material for orthopedic implant applications. Further, the biocompatibility and antibacterial properties of tantalum coatings have been reported. Tantalum-based thin films exhibited antimicrobial potential against several microorganisms, such as Staphylococcus aureus, Staphylococcus epidermidis [1, 2]. In addition, the anti-adhesive properties of Ta-based materials have been analyzed [3].

Due to their structural stability and biocompatibility, non-degradable polymer materials have been applied in a wide range of medical devices, in particular, as bearing surfaces in hip implants, vascular grafts or catheters and ocular implants [4, 5].

Hernioplastic mesh prostheses are commonly used for substitution of aponeurotic and muscle tissue. Polypropylene is probably the most widely used prosthetic material in mesh repair owing to its low cost, non-biodegradability and excellent incorporation [6]. The main properties required for intraperitoneal meshes are mechanical stability, adhesion prevention, good incorporation to prevent...
recurrence, shrinkage and mesh migration, as well as lack of inflammation and allergic reactions. The
currently used polypropylene meshes induce severe chronic inflammatory reactions over a long-term
period [7]. These processes lead to scarring and have a negative effect on the connective tissue and
abdominal walls. Moreover, effects have been reported on the apoptosis rates due to the polymer
destruction and their degradation products, resulting in carcinogenic potential based on apoptosis rates.
In addition, the inflammatory reaction can lead to adhesions or fistula formation [8]. There is strong
association between adhesions and bowel obstruction, infertility and chronic pain [9]. Obviously,
further research is needed to improve the mechanical and anti-adhesive properties of modern meshes.
It is known that the biocompatibility of polymer surfaces might be improved by surface modification.
Several problems are associated with the magnetron discharge deposition of coatings on plastic
substrates. First, the plastic melts easily, so that to avoid this process the coatings should be deposited
at a low power of the magnetron discharge. Secondly, internal stresses in the films lead to deformation
of the coatings due to the softness of the plastic materials. Under some deposition conditions,
delamination is observed as a result of the very high internal stresses in the films.

The research presented was aimed at studying the effect of deposition process parameters on the
structural and mechanical properties of Ta, Ta2O5 and TaON films on polypropylene meshes intended
for hernioplasty application.

2. Materials and methods
Polypropylene plates and meshes were used as substrates (Fig. 1). A wide range of pressures were
applied to optimize the deposition process and the optimal technological conditions were determined
allowing one to avoid plastic and coatings deformation during the deposition process.

The samples were cleaned in an ultrasonic bath following a standard technique. Then, an ion source
(Radical type) was used to clean the sample surface before deposition [10]. The deposition of Ta,
Ta2O5 and TaON coatings by magnetron sputtering was performed in a high-vacuum pumping system
with a base pressure of about 1×10⁻⁵Pa. A tantalum target with a diameter of 170 mm was used. The
magnetron discharge power was 4 – 5 kW. Also, an ICP source for oxygen activation with RF power
of up to 1 kW was applied. The ion cleaning process parameters were \( p_N = 1.2 \times 10^{-2} \text{ Pa} \), oxygen mass
flow rate \( q = 45 \text{ sccm} \). The main deposition process parameters were \( p_A = 1.2 \times 10^{-2} \text{ Pa} \), magnetron
voltage \( U_m = 465 – 480 \text{ V} \), magnetron current \( I_m = 2.3 – 3.4 \text{ A} \), Ta2O5 deposition oxygen flow
\( q_O = 20 \text{ sccm} \), TaON deposition nitrogen flow \( q_N = 16 \text{ sccm} \), oxygen flow \( q_O = 4 \text{ sccm} \).

The coatings thickness and adhesion properties were evaluated by standard techniques. The values
measured of the coatings thickness were 1.1 μm (Ta), 1.05 μm (Ta2O3) and 0.8 μm (TaON). The
surface morphology and topography were observed by a JSM-7100F electron scanning microscope
(SEM, JEOL, Japan). The elemental distribution and chemical composition of the coatings were
analyzed by energy dispersive X-ray (EDX) spectroscopy (Oxford Link ISIS 300). X-ray
photoelectron spectroscopy (XPS) measurements were carried out using an ESCALAB MkII
apparatus (VG Scientific, UK). The mechanical tests of the Ta-based coated samples to evaluate the
Vickers hardness parameters and elastic modulus were performed on a G200 Nano Indenter (KLA,
USA).

3. Results and discussion
Figure 2 shows SEM images of Ta, Ta2O5 and TaON coatings deposited by magnetron sputtering. The
coatings cross-section was smooth without delamination. The EDX spectra revealed the presence of
the main characteristic elements tantalum (Ta), oxygen (O) and nitrogen (N).
The compositional analysis of the Ta, oxide Ta$_2$O$_5$ and oxynitride TaON coatings by means of XPS revealed the photoelectron spectra of Ta4f, O1s, N1s coatings as previously observed [10]. The spectrum included the photoelectron lines of Ta (4f7/2) and Ta (4f5/2). The Ta$^{5+}$ signals were detected at the binding energies of 26.8 eV and 28.7 eV. The O1s high-resolution spectrum exhibited a peak at the binding energy position of 530.9 eV associated with the Ta-O chemical bond. The N1s peak was detected at the binding energy of 396.2 eV assigned to the Ta-N chemical bond. This peak is generally considered to be evidence of O atoms replacement by N atoms in the Ta$_2$O$_5$ crystal lattice [11]. Also, a weak N1s peak at the binding energy of 398.0 eV was observed corresponding to the Ta-N-O chemical bonds [12].
Figure 2. SEM images and EDX spectra of Ta (a), Ta$_2$O$_5$ (b), and TaON (c) deposited coatings.

The coatings’ mechanical properties are strongly correlated with their microstructures, phase and chemical composition. The values of the hardness ($H$) and Young’s modulus ($E$) of the Ta-based coatings compared with the polypropylene substrates are presented in Fig. 3.

Figure 3. Hardness ($H$) and Young’s modulus ($E$) of the Ta-based coatings compared with the polypropylene substrates.

The improvement of the coated materials’ properties in comparison with the uncoated polymers was analyzed previously [7, 13]. The Ta-based coatings demonstrated a relatively high hardness and Young’s modulus, corresponding to a high elastic recovery and a high resistance to cracking [14], which makes these materials highly attractive for hernioplasty applications. The variations in hardness
and Young’s modulus under irradiation processes were previously analyzed [15]. Both the hardness and the Young’s modulus increased within micrometers-depth in the irradiated samples.

4. Conclusion
Ta-based coatings deposited by magnetron sputtering were found to improve the mechanical characteristics and biocompatibility of the polypropylene materials. The results demonstrated the effect of Ta-based coatings composition on their properties. The coated samples exhibited higher nano hardness and elasticity values, significantly exceeding the values of untreated polypropylene. Thus, optimal deposition parameter were achieved. The Ta-based films possessed properties favorable in view of potential prosthetic applications in hernioplasticsurgery.

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