

Polyelectrolyte multilayer deposition on modified Phynox substrates

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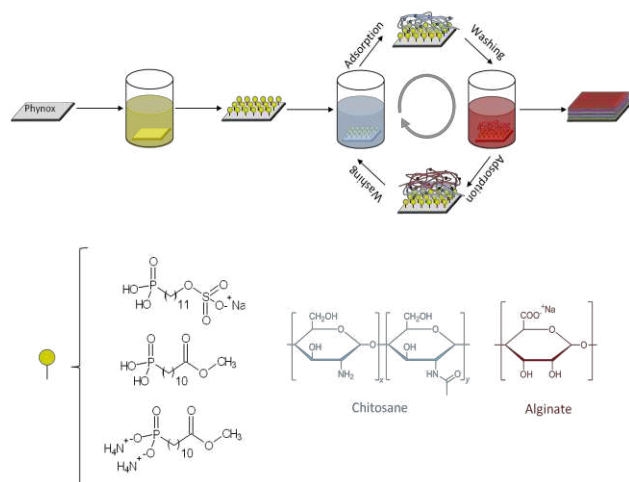


Fig. 1: Schematic representation of the work methodology

Phynox is an austenitic cobalt – chromium alloy (AFNOR designation K13C20N16Fe15D07) with a great variety of chemical, physical and biochemical properties such as resistance to corrosion and high passivity in contact with human tissues¹. In combination with its remarkable bulk properties, several Phynox applications, in particular the biomedical ones (medical instruments, stents, pacemaker electrodes, implants, ...) ², require specific surface properties that can be imparted with suitable surface functionalizations of the Phynox protective oxide layer. The tendency of organophosphonic acids to form monolayers on metal oxide surfaces³⁻⁵ and their important resistance to homocondensation and hydrolysis^{6,7} make them particularly interesting candidates for such oxidized surface functionalizations.

Phynox surface modification by organophosphonic acids grafting and their potential applications in the biomedical field has been reported in previous studies in the literature^{1,8,9}. The use of covalently grafted organophosphonic acids as polymerization initiators in atom transfer radical polymerization (ATRP), which is gaining increasing importance, has proven its high capability to build strongly adherent thin films and/or polymer layers on the surfaces to impart adequate properties to the surfaces^{9,10}. On the other hand, organophosphonic acids have been also used as adhesion promoters in layer-by-layer (LbL) assembly¹¹. Since its introduction by Decher¹², the formation of LbL assembly of polyanions and polycations into multilayers has become a very popular method for the formation of functional thin films. The popularity of this method lies in its simplicity. Polymers carrying charged functional groups (such as chitosane and alginate) when dissolved in adequate solvent are called polyelectrolytes. They can be deposited on charged surfaces by successive electrostatic adsorptions. So far, to our knowledge, the formation of LbL on Phynox substrates hasn't yet been studied in the literature.

In the first part of this work, the feasibility of polyelectrolyte multilayer deposition on modified Phynox substrate will be demonstrated. In the second part, the importance of the interface between the Phynox surface and the polyelectrolyte layers will be enhanced and showed as a primordial parameter to control.

A phosphonic acid functionalized with a sulfate terminal group has been successfully synthesized and grafted on Phynox substrates. This grafting allows the presence of negative charges at the surface of Phynox, which becomes therefore a suitable platform for polyelectrolyte multilayer deposition with chitosane and alginate. Water static contact angle analyses showed a typical LbL behavior with a variation of the water static contact angle depending on the terminal polyelectrolyte layer. The presence of LbL has been confirmed by X-ray photoelectron spectroscopy (XPS) and the electrochemical behavior has been studied by cyclic voltammetry (CV) and polarization curves (LSV). However these techniques also revealed degradation/desorption of these polyelectrolyte layers due to a poor quality grafting of the adhesion promoter.

To assess the influence of the interface, and therefore the grafting quality of the adhesion promoter, other phosphonic acid derivatives have been synthesized and grafted on Phynox substrates. This is based on previous studies on nickel substrates, in which, the hydrolysis of the ester function of grafted 11-methylundecaneatephosphonic acid to generate negative charges appeared as a good technique for the polyelectrolyte layer deposition.

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