

Morphology Tuning of Chitosan Films via Electrochemical Deposition on Metallic Substrates

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Statement of Purpose: Chitosan is a natural cationic polysaccharide with a wide range of applications, ranging from cell culture substrates (skin, bone, cartilage and vascular grafts) to drug delivery systems [1]. Its use has been proposed for novel local therapeutic approaches in orthopedics and orthodontics, based on amino groups availability. The presence of $-NH_2$ on chitosan backbone provides a versatile carrier for biological active species and triggers its solubility in aqueous solutions as well. Recently, electrochemical deposition of chitosan via cathodic polarization has been proposed, based on reduction reactions that lead a local increase of pH resulting in chitosan film deposition on electrically conductive substrates [2]. Cathodic electrodeposition represents a powerful surface modification technique for biopolymer deposition since it allows an easy control of process parameters which affect the quality of obtained films in terms of their homogeneity and thickness. Here, we show the effects of anionic species selection and concentration on morphology of deposited coatings, resulting in a novel and effective technique to produce porous films with controlled dimensions.

Methods: Titanium specimens (CP Ti grade 2 $\Phi = 12$ mm, 0.5 mm thickness) were used following acid etching (HF 3%, HNO_3 20%) and subsequently washing in acetone and distilled water. Four stock solutions of 10 g L^{-1} of chitosan (practical grade, deacetylation > 75%) in acid water were prepared, according to the following molarities: 0.575M phosphoric acid H_3PO_4 , 2.62M CH_3COOH , 0.0961M malonic acid $CH_2(COOH)_2$ and 0.143M citric acid monohydrate $C_6H_8O_7H_2O$. Each acid solution has been stirred, centrifuged and then aqueous solutions of 1g/l of chitosan were prepared. Cathodic deposition on titanium specimens has been performed in galvanostatic conditions at two different current densities ($j = 5mA\ cm^{-2}$ and $j = 20mA\ cm^{-2}$) up to 4 min. Morphological and structural analysis of the coatings have been performed after rinsing in deionized water and drying overnight. Coatings have been weighed and their morphology observed by optical stereomicroscope and Scanning Electron Microscopy. Dry specimens after cathodic electrodeposition were immersed for 1h in a solution of ethanol at 0.025% of fluorescein sodium salt powder (Sigma-Aldrich F6377 - CAS Number 518-47-8), rinsed in millipore water and observed with optical microscope, equipped with fluorescence filter. To improve films stability, two cross-linking agents have been used: sodium tripolyphosphate (TPP, $Na_5P_3O_{10}$, 10% w/v) and sodium phosphate (Phos, $NaH_2PO_4 \cdot H_2O$, 10 and 30% w/v). Specimens were immersed in cross-linking solutions, at 4 °C for 4h, 8h and 24h. Cross-linked samples were immersed in PBS (Dulbecco's phosphate buffered saline) at 37 °C. Specimens were weighed at

different time points (up to 21 days).

Results: Cathodic electrodeposition of acidic solutions of 1g/l of chitosan led to a different amount of deposited chitosan: different acid anions resulted in a different deposited quantity with similar polarization parameters (current density and time).

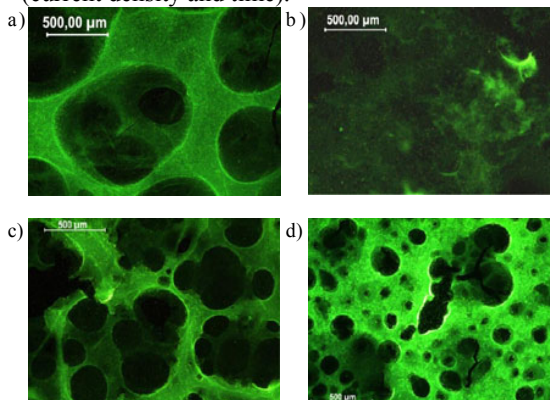


Fig 1 Optical fluorescence images of coating surfaces after cathodic electrodeposition with $j=5mA\ cm^{-2}$ for 2 minutes of aqueous solutions of 1 g L^{-1} of chitosan: (a) acetic acid pH 4 (b) 0.3% phosphoric acid, (c) 0.1% malonic acid and (d) 0.3% of citric acid

In Fig.1 the effect of bath composition on chitosan film morphology is shown: pores show a regular round morphology with different average dimension. Films deposited from acetic acid bath resulted in larger pores whereas malonic acid and citric acid show smaller pores; on the contrary, phosphoric acid resulted in a compact and homogeneous film. Moreover, by using malonic acid, an increase in pore interconnection in comparison with citric acid is evident (Fig. 2, c and d). Stability tests in PBS showed the swelling of treated coatings after few hours of immersion and an improved stability after cross-linking in both solutions (TPP and Phos) up to 21 days.

Conclusions: An easy tuning of chitosan coating morphology has been obtained by modifying electrolytic bath and current densities. Obtained films show an interesting porosity, both in terms of dimensions and interconnection. Further studies as self standing scaffolds of the obtained structures are in progress.

References

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Acknowledgments

Authors thank Istituto Italiano di Tecnologia for the economic support provided to AC and RC. LA and LD thank MIUR - FIRB Futuro in ricerca (Surface-associated selective transfection - SAST, RBFR08XH0H) for the economic support.