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## How alkali-activated Ti surfaces affects the growth of tethered PMMA chains: a close-up study on the PMMA thickness and surface morphology

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### *Abstract*

The alkali-activation of titanium (Ti) surfaces performed in a heated sodium hydroxide (NaOH) aqueous solution, results in a porous layer rich in hydroxyl (OH) groups, the structure and porosity of which strongly depend on the reaction time and NaOH concentration used. In this study, a polymerization initiator is covalently grafted on the alkali-activated Ti substrates by using a phosphonic acid as coupling agent and the resulting surfaces are used as scaffolds to drive the growth of tethered poly(methyl methacrylate) (PMMA) chains via a surface initiated atom transfer radical polymerisation (SI-ATRP).

A close-up investigation of how five different treatment times (1 h, 3 h, 6 h, 12 h, and 24 h) and NaOH concentrations (0.1 M, 0.5 M, 1 M, 2 M, and 5 M) affect the final PMMA morphology and thickness are here presented.

**Keywords:** alkali treatment; ATRP; Eurasia 2018; PMMA; Ti-PMMA interface; titanium.

## 1. Introduction

Modification of the metal surface properties using organic layers is a field of great interest in many industrial fields, such as automotive, electronics and biomedical ones. Indeed, several interfacial properties, such as adhesion, wetting, elasticity and biocompatibility can be tailored.<sup>1</sup> Polymeric coatings can be used in biomaterials field to achieve specific properties to improve the osseointegration between the implant and the surrounding bone<sup>2,3</sup> and/or producing antibacterial or protein-repellent surfaces.<sup>4,5,6</sup>

Metal-polymer adhesion includes many types of interactions, ranging from weak interactions to covalent bonds. Typically due to the physical adsorptions of the polymer chains on the metal substrates, the first ones include the electrostatic and the hydrophobic interactions, as well as the hydrogen bonding.<sup>7,8</sup> These techniques – which include chemical/physical deposition techniques (i.e. spin-coating, dip-coating or spray-coating), layer-by-layer deposition and absorption from solution (i.e. self-assembly monolayers) – allow a simple fabrication of polymer-coated surfaces. Nevertheless, being their durability strongly related to the nature of the polymer-metal interface, the long-term stability of the system is tremendously affected by delamination phenomena caused by the weak adhesion existing between the organic layer and the metal.<sup>9</sup>

In order to enhance the life-time and stability, adhesive layers made of grafted polymers, have been placed between the metal substrate and the polymer coating to strengthen their adhesion.<sup>10,11,12</sup> Further, in our recent work<sup>13</sup> a strategy allowing the development of hybrid-layered structures consisting of thick, stable and biocompatible poly(methyl methacrylate (PMMA) grown on previously activated-Ti substrates was described.

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<sup>1</sup> L. Wu and J. Baghdachi, *Functional Polymer Coatings: Principles, Methods, and Applications*, vol. 12. John Wiley & Sons, 2015.

<sup>2</sup> J. E. Raynor, J. R. Capadona, D. M. Collard, T. A. Petrie, and A. J. García, *Biointerphases*, vol. 4, no. 2, pp. FA3–FA16, 2009.

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<sup>11</sup> K. Shimizu, K. Malmos, A. H. Holm, S. U. Pedersen, K. Daasbjerg, and M. Hinge, *ACS Applied Materials & Interfaces*, vol. 6, no. 23, pp. 21308–21315, 2014.

<sup>12</sup> K. Shimizu, K. Malmos, S.-A. Spiegelhauer, J. Hinke, A. H. Holm, S. U. Pedersen, K. Daasbjerg, and M. Hinge, *International Journal of Adhesion and Adhesives*, vol. 51, pp. 1–12, 2014.

<sup>13</sup> O. Alageel, M.-N. Abdallah, Z. Y. Luo, J. Del-Rio-Highsmith, M. Cerruti, and F. Tamimi, *Dental Materials*, vol. 31, no. 2, pp. 105–114, 2015.

<sup>14</sup> M. Reggente, P. Masson, C. Dollinger, H. Palkowski, S. Zafeiratos, L. Jacomine, D. Passeri, M. Rossi, N.E.; Vrana, Pourroy, G.; Carrad   A., *ACS Appl. Mater. Interfaces* 2018, 10, 5967–5977

It consists in a three-step methodology (**Scheme 1**). Firstly, Ti substrates are activated; secondly, a phosphonic acid derivative used both as coupling agent and polymerization initiator, is anchored on the activated substrates through a “grafting from” method. Thirdly, surface initiated atom transfer radical polymerization (SI-ATRP) is employed to grow tethered PMMA chains.



**Scheme 1:** Procedure followed to grown tethered PMMA chains on alkali-activated Ti surfaces using phosphonic acids as anchoring groups via surface initiated atom transfer radical polymerization (SI-ATRP).

This activation, performed in a NaOH solution, leading to a nanostructured sodium titanate interlayer with an open microporosity, was found to drive the growth of the polymer chains along its pillared structure enhancing the development of the polymer layer. This latter is covalently linked to the metal substrates by grafting phosphonic acids, leading to the creation of strong Ti-O-P bonds by reacting with the hydroxyl groups on the activated Ti surfaces (see **Scheme 1**). In this work, we investigate how different NaOH concentration and treatment time affect the polymer growth in terms of morphology and thickness.

## 2. Experimental section

### 2.1 Sample preparation

Titanium (Ti) disks (20 mm in diameter and 3 mm thick), cut from a commercially pure grade 4 Ti rod, and grade 2 Ti sheets ( $10 \times 10 \times 0.5 \text{ mm}^3$ ) were mechanically polished with 600, 1000, 2400 and 4000 grit silicon carbide (SiC) papers. Successively, they were treated with colloidal silica suspension (particle size:  $0.05 \mu\text{m}$ ) to achieve bright reflective, mirror-like surfaces. Then, all the samples were cleaned by ultra-sonication in acetone, ethanol and deionized water, 10 min each solvent, to remove the residues of the mechanical treatment.

### 2.2 Alkaline treatment of titanium surfaces

Alkaline treatments of the Ti substrates were performed by immersing Ti disks into a Teflon beaker containing an aqueous NaOH solution, kept at  $80^\circ\text{C}$ .<sup>14</sup> Five reaction times (1 h, 3 h, 6 h, 12 h and 24 h) and five NaOH concentrations (0.1 M, 0.5 M, 1 M, 2 M and 5 M) were employed and their effects on the resulting Ti morphology and structure were investigated.

<sup>14</sup> Zhang, K.; Li, J.-A.; Deng, K.; Liu, T.; Chen, J.-Y.; Huang, N., *Colloids Surf., B* 2013, 108, 295–304.

### 2.3 Surface-initiated atom transfer radical polymerization (SI-ATRP) of PMMA chains

The elsewhere reported SI-ATRP of methyl methacrylate was used to grow PMMA chains covalently linked on alkali-activated Ti surface.<sup>13,4</sup> Firstly, the grafting reaction of a home-made polymerization initiator, the bromoisobutyrateundecyl-1-phosphonic acid<sup>15</sup>, was performed in an aqueous solution heated at 100 °C for 24 h. Secondly, the polymerization reaction, which lasted for 24 h, was carried out in anisole under an argon atmosphere at a temperature of 35°C. Malononitrile was used as activator to enhance the polymerization rate.<sup>16</sup>

### 2.4 Surface and cross-section characterizations

**Chemical characterizations.** The reactions were followed by attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FTIR) and X-ray photoelectron spectroscopy (XPS). The former analysis was performed using a Spectrum Two PerkinElmer spectrometer. XPS spectra reported were recorded with a MULTILAB 2000 (THERMO VG) spectrometer equipped with an Al K $\alpha$  anode ( $h\nu$  = 1486.6 eV). The C 1s peak at 284.6 eV was used to correct charging effects.

#### Morphological characterizations.

The surface morphology was characterized by scanning electron microscopy (SEM) using a JEOL 6700 electron microscope equipped with an energy dispersive X-ray spectroscopy analysis (EDS-X). In addition, cross-sectional views were observed by SEM analysis using either a CrossBeamR Workstation (FIBSEM) AURIGA-Zeiss 405 Microscope equipped with a Quantax EDS-X system or a Zeiss GeminiSEM 500 SEM fitted with an EDS-X system from EDAX (Octane Elite SDD detector + TEAM software). In the latter case, the sample's cross-section was firstly prepared using an ion beam cross-polisher (Hitachi IM4000+). The samples were cut with a metallographical saw and an edge from the backside was polished with a 25° bevel (SiC P1000 paper) to reduce the thickness of Ti to be polished by the ion beam. The cross polishing was then performed from the backside (6 keV, Ar). By this way, the organic material was protected by the Ti itself and very few was exposed to the ion beam.

## 3. Results and discussion

### 3.1 Alkaline treatment of titanium surfaces

First, Ti Gr. 4 disks were mechanically polished, in order to reduce its surface roughness and obtained a mirror-like surface. Then, the mechanically polished Ti surfaces were activated using an alkali treatment performed in a NaOH solution. The aim of this study was to find the best conditions ensuring a high content of surface hydroxyl groups together with a desired surface roughness. Indeed, as already reported<sup>2, 17, 18</sup> this alkali treatment etched the Ti samples producing superhydrophilic amorphous sodium titanate layer with a nanostructured open porosity. In the following sections, the effect of different treatment times and NaOH concentrations were investigated and discussed.

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<sup>17</sup> Kim, H.M.; Miyaji, F.; Kokubo, T.; Nakamura, T; *Journal of the Ceramic Society of Japan*, vol. 105, no. 1218, pp. 111–116, 1997

<sup>18</sup> Carradò, A., Perrin-Schmitt, F., Le, Q. V., Giraudel, M., Fischer, C., Koenig, G., Morlet, A. (2017). *Dental Materials*, 33(3), 321-332

### 3.1.1 Effect of the alkali time treatment

The goal was to find the time required to induce an amount of OH groups on the Ti surfaces ensuring a good grafting of the initiator molecules. A 2 M concentrated NaOH solution (already used to favour the adsorption of collagen on Ti substrates<sup>19</sup> and a temperature of 80 °C were chosen and the effect of five treatment times (1 h, 3 h, 6 h, 12 h and 24 h) was studied.

In **Figure 1a** the FTIR spectra of the alkali-activated Ti substrates after each analysed reaction time are reported. The broad band at 3600 cm<sup>-1</sup> and 3100 cm<sup>-1</sup> is assigned to the fundamental stretching vibrations of different OH hydroxyl groups<sup>20,21</sup>. The shoulder around 958 cm<sup>-1</sup>, whose intensity increases for longer treatment time, indicates the presence of Ti-OH species. Finally, the peak between 650 cm<sup>-1</sup> and 400 cm<sup>-1</sup>, whose width decreases by diminishing the treatment time, is assigned to the Ti-O-Ti stretching vibrations. It can be concluded that the shorter the alkali treatment time, the lesser the quantity of oxide.

The surface morphology of the substrates subjected to the alkali treatment mentioned above, were investigated by SEM (Figure 1). It has been shown that shorter treatment times result in an inhomogeneous microporous layer. As a result, shorter treatment times result in an inhomogeneous microporous layer. Indeed, the alkali treatment leads to the formation of a hierarchical porous layer. Indeed, the alkali treatment leads to the formation of a hierarchical porous layer, with a pore size ranging between 50 nm to 200 nm, consisting of regular pillared and cone-shaped features covering the Ti surface (**Figure 1**). The surface morphology of the sample treated for 1 h is characterised by a nanostructured network with interconnected pillars of a few tenth of nanometers in width and a high open porosity (**Figure 1b**). Whereas, an increase of the treatment time produces a reduction of the specific surface: the pillars become thicker and the porosity less interconnected (**Figure 1c-f**). In particular, **Figure 1c** refers to a surface treated for 3 h; the surface features obtained after a 6 h-NaOH treatment are depicted in **Figure 1d**. A further increase of the treatment (12 h) produces a less branched network composed of facets rather than pillars, as highlighted in **Figure 1e**.

For longer time treatment (24 h, reported in **Figure 1f**), the typical surface features of the layer do not uniformly cover the Ti surfaces suggesting that a too long reaction time causes an agglomeration of the already “etched/reacted” material resulting in a more compact structure. Whereas, it was pointed out that, maintaining a constant 2 M NaOH concentration, for treatment time longer than 6 h, the surface porosity decreases by increasing the time. Compared to previously reported results, in which more concentrated solutions (5 M and/or 10 M) are generally employed<sup>22,23,186</sup>; these observations are in agreement with the hypothesis that, for the chosen concentration, there is a threshold time above which the produced interlayer collapses. Instead, for more concentrated solutions (5 M and 10 M), even after a treatment of

<sup>19</sup> Zhang, K.; Li, J.-A.; Deng, K.; Liu, T.; Chen, J.-Y.; Huang, N., *Colloids Surf., B* 2013, 108, 295–304

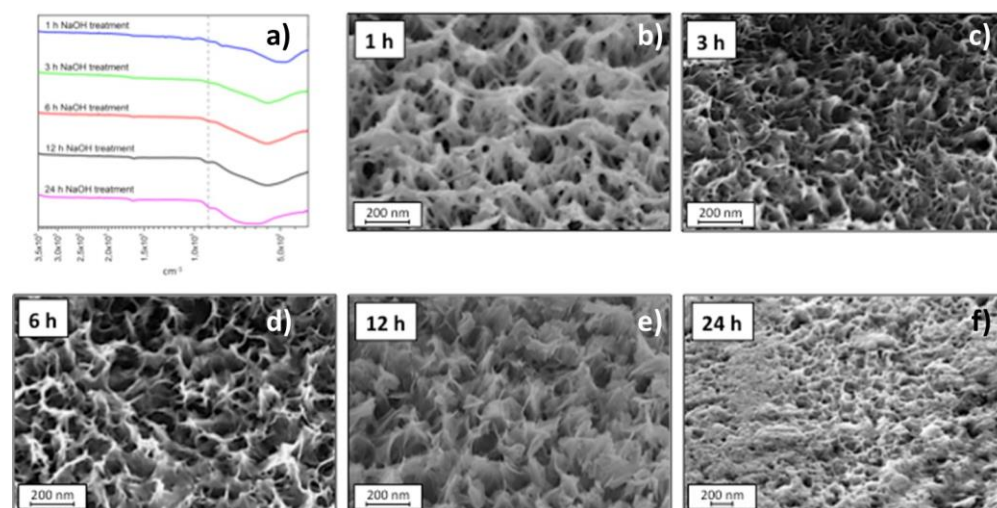
<sup>20</sup> Guerrero, P. Mutin, and A. Vioux, *Chemistry of Materials*, vol. 13, no. 11, pp. 4367–4373, 2001

<sup>21</sup> V. Vergnat, T. Roland, G. Pourroy, and P. Masson, *Materials Chemistry and Physics*, vol. 147, no. 1, pp. 261–267, 2014

<sup>22</sup> Kim, H.M.; Miyaji, F.; Kokubo, T.; Nakamura, T; *Journal of the Ceramic Society of Japan*, vol. 105, no. 1218, pp. 111–116, 1997.

<sup>23</sup> S.I. Tanaka, H. Tobimatsu, Y. Maruyama, T. Tanaki, and G. Jerkiewicz, *ACS Applied Materials & Interfaces*, vol. 1, no. 10, pp. 2312–2319, 2009.

24 h, there are more NaOH species available to react creating a porous layer uniformly distributed on the surface.<sup>24,25</sup>



**Figure 1.** a) ATR-FTIR spectra of the Ti surfaces activated in a 2 M concentrated NaOH solution for 1 h (blue), 3 h (green), 6 h (red), 12 h (black) and 24 h (pink). Morphologies of the Ti surfaces after an alkali treatment in a 2 M concentrated NaOH aqueous solution for: b) 1 h; c) 3 h; d) 6 h; e) 12 h and f) 24 h.

### 3.1.2 Effect of the alkali concentration

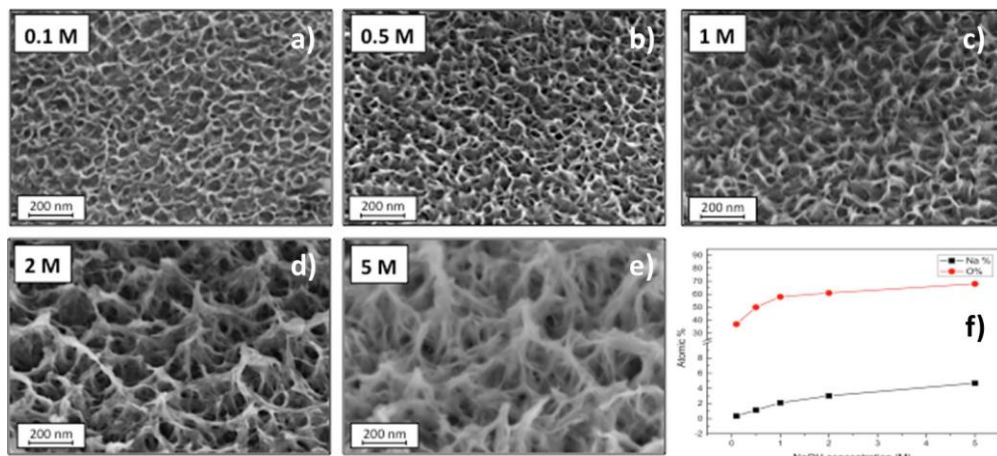
By fixing a treatment time of 1 h, which ensures a higher open porosity of the surface, the effect of different NaOH concentration was studied. **Figure 2a** and **Figure 2b** show the surface morphologies achieved employing 0.1 M and 0.5 M NaOH concentrations, respectively. They give rise to a sodium titanate layer appearing less structured and thinner compared to that obtained with a 1 M concentrated solution (**Figure 2c**).

A solution of 5 M (**Figure 2e**) produces a thicker interconnected layer with pillars wider even compared to those obtained after a treatment with a 2 M concentrated NaOH solution (**Figure 2d**). This is also confirmed by the elemental analysis performed by EDS-X measurements that highlighted an increase in the oxygen (O) and sodium (Na) content as the concentration increases (**Figure 2f**).

<sup>24</sup> M. Wei, H.-M. Kim, T. Kokubo, and J. Evans, “*Materials Science and Engineering: C*, vol. 20, no. 1, pp. 125–134, 2002.

<sup>25</sup> L. Jonášová, F. A. Müller, A. Helebrant, J. Strnad, and P. Greil, *Biomaterials*, vol. 25, no. 7, pp. 1187–1194, 2004.

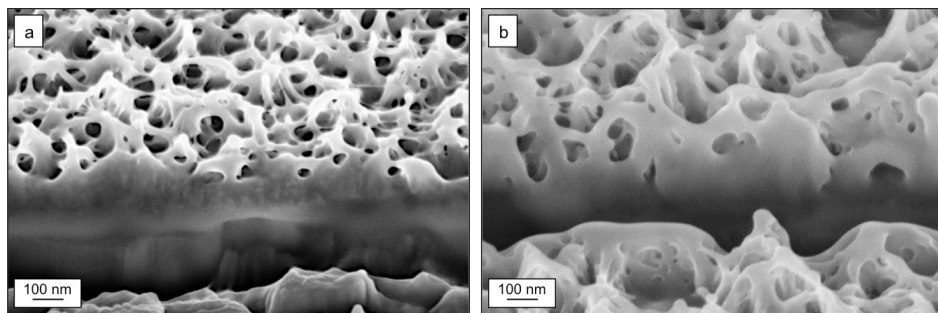




**Figure 2.** SEM micrographs of Ti surfaces after an alkali treatment of 1 h in: a) 0.1 M NaOH concentrated solution; b) 0.5 M NaOH concentrated solution; c) 1 M NaOH concentrated solution; d) 2 M NaOH concentrated solution; e) 5 M NaOH concentrated solution and f) Variation of the Na and O atomic percentage (with errors bar of 10%), determined by EDS-X measurements, as function of the NaOH solution concentration.

### 3.2 Ti surface functionalization

The hierarchical structure of the microporous layer, produced by the alkali treatment, was successively used as a scaffold able to drive the following polymerization in order to achieve thick and porous polymer coating. **Erreur ! Signet non défini.** For this purpose, it was necessary to have a highly open structure with a few hundreds of nanometers thickness. Indeed, a closer and more compact structure could limit the further growth of the polymer brushes.

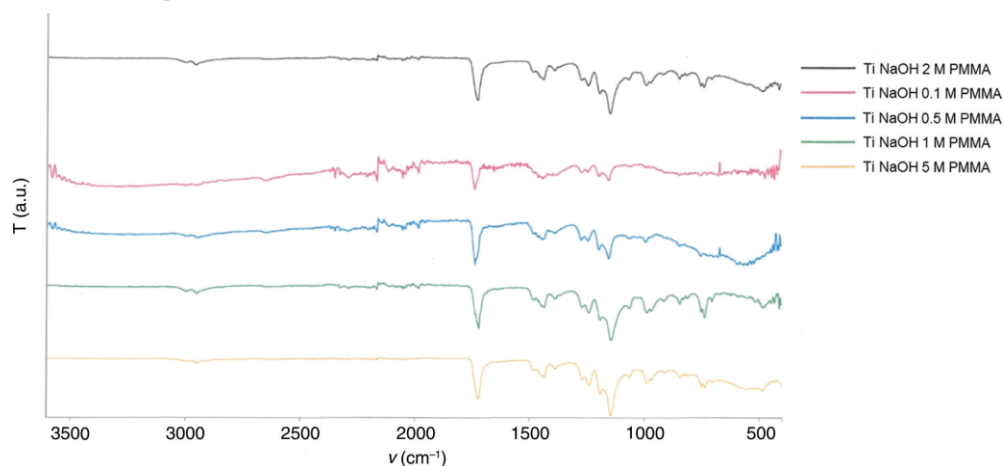


**Figure 3:** a) cross-section of a 2 M 1 h alkali-activated Ti surface; b) cross-section of a 5 M 1 h alkali-activated Ti surface;

For this reason, a time of 1 h and two concentrations (2 M and 5 M) of the NaOH treatment were selected and their effect on the surface morphology and thickness of the PMMA layer further investigated. **Figure**



3 reports the cross-sections titanate layer thickness of the so-treated Ti substrates (hereafter labelled 2M 1h alkali-activated Ti (**Figure 3a**) and 5M 1h alkali-activated Ti (**Figure 3b**)) obtained using focus ion beam (FIB) coupled with SEM.



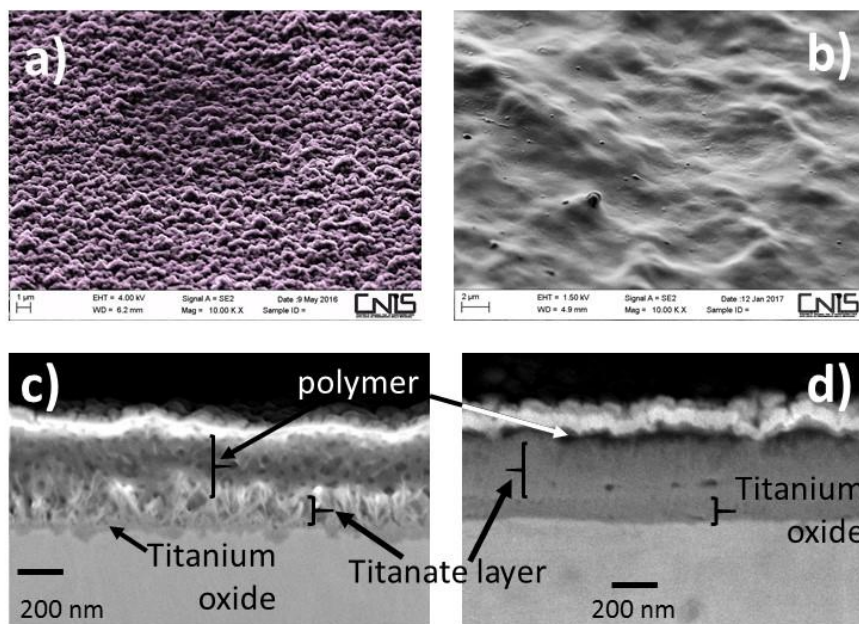
**Figure 4:** FTIR spectra of the PMMA layer grown on 0.1 M–5 M alkali-activated Ti surfaces.

FTIR spectra on the PMMA coated on functionalized Ti surface after ATRP, exhibit the characteristic lines of the PMMA (**Figure 4**). However, for small concentrations of NaOH (0.1 M and 0.5 M) the signal-to-noise ratio is weak and the peaks are poorly defined. For the higher concentrations of NaOH (1 M, 2 M and 5 M), the characteristic peaks of PMMA are well defined.

**Figure 5** shows the morphology and the cross section of the PMMA layer obtained after growing the chains from a Ti substrate activated in 2M NaOH (**Figure 4a** and **4c**) and in 5 M NaOH (**Figure 4b** and **4d**). **Figure 5a** and **Figure 5b** highlight that the smoothest surface was obtained after a 5 M NaOH activation.

When Ti was submitted to a 2M NaOH treatment, the surface looks embossed and very irregular. The cross-section observations (**Figure 5c** and **5d**) reveals three different layers: titanium dioxide in contact with titanium, then the sodium titanate and at the top the polymer. The width of each of them varies a lot when comparing the two cases. When the NaOH solution is the less concentrated (2M), the porous structure of the titanate layer is clearly visible. The titanate was grown on a thin layer of titanium oxide and has about 200 nm in thickness. The polymer layer is of about 300–400 nm thick and contains closed porosity. Furthermore, the polymer and the titanate interlayer are intricately linked showing that the polymer has grown inside the titanate pillared structure.

When Ti was submitted to 5 M NaOH treatment, the porous structure of sodium titanate disappeared. The growth rate of the titanate increased with respect to the growth rate in 2M NaOH due to the highest concentration of sodium ions. A dense titanate layer replaces the pillared structure. Furthermore, the polymer layer is very thin. Indeed, the surface available for grafting is strongly decreased, and the steric hindrance prevents the polymer chains to grow. Furthermore, the titanate contains probably less hydroxyls groups due to the highest pH that is less favourable to the polymer growth.



**Figure 5:** a-b) Surface morphology of a polymer layer grown starting from a Ti substrate activated in 2M and 5 M concentrated NaOH solution for 1 h and functionalized with the bromoisobutyrateundecyl-1-phosphonic acid ATRP initiator; c and d) SEM and cross-section cross polisher of PMMA layer grown on 2M (c) and 5 M (d) alkali activated Ti surfaces. The copper thin layer deposited onto the surface (bright line) is good eye-guide to see the polymer limit.

#### 4. Conclusion

The “grafting from” process used to create covalent bond between Ti and PMMA chains implies the formation of strong Ti–O–P bonds by reacting the hydroxyl groups on the activated Ti surfaces and the phosphonic anchor group of the initiator.

The alkali-activation of Ti surfaces performed in a heated sodium hydroxide aqueous solution, results in a porous layer rich in hydroxyl (OH) groups. The structure and porosity of which strongly depend on the reaction time and NaOH concentration used. Effectively, the activation process leads to a nanostructured sodium titanate interlayer with an open microporosity with pillared structure. This microporosity and the pillared structure drive the growth of the polymer chains during the ATRP process.

The best experimental conditions for the alkali treatment correspond to a 2 M concentration and a reaction time of 1 h. Under these conditions a thick PMMA layer of about 300–400 nm was obtained. Furthermore, the polymer chains and the titanate interlayer are intricately covalently as well as mechanically; it strengthens their adhesion and may prevent the delamination phenomena.

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