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Self-assembled ultrathin films of cellulose nanofibrils and poly(o-ethoxyaniline

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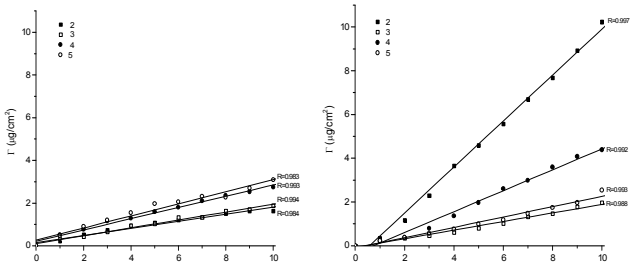
Abstract – Ultrathin films of poly(o-ethoxyaniline) (POEA) alternated with cellulose nanofibrils (CnF) were successfully produced by self-assembly at different pH values and investigated by atomic force microscopy (AFM) and ultraviolet-visible (UV-Vis) spectroscopy. Results show that it was possible to build up films by alternating POEA and CnF layers with relatively precise architectural control by controlling the number of layers and pH. Comparison of alternated layers of POEA and CnF with multi-immersions of POEA at different pH values, as measured by the ratio between slopes of the straight lines of deposited amount of polymer versus the number of self-assembled layers, shows that alternate deposition at pH 2 has a four-fold increase in the slope. Alternatively, at pH 5 there is no significant difference whether the deposition is alternated (POEA/CnF) or not (POEA).

Cellulose nanofibrils have recently gained scientific attention because of their remarkable physical and rheological properties [1-2]. Similarly, conducting polymers offer unique combination of properties of both metals and plastics, which has enabled applications in devices such as sensors and biosensors, batteries, light emitting diodes and electroluminescent displays, and coatings [2]. In most of these applications, the polymer is used in the form of thin films which are usually produced by SA, spin coating, Langmuir-Blodgett or casting [1]. Therefore, control of film architecture is of paramount importance to attaining film reproducibility, durability and performance. In this work, nanostructured multi-layer thin films of POEA and CnF were successfully produced by SA at different pH values, and their structure was investigated by AFM and UV-Vis Spectroscopy.

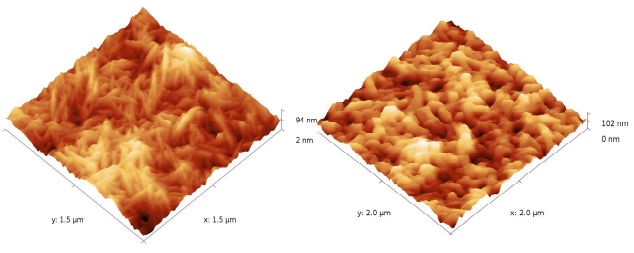
Fig.1 shows the amount of material deposited (Γ) for POEA alternated with CnF is much greater than that for POEA alone, indicating that CnF is also being alternately deposited at the various pH investigated. When multi-layer films of POEA are built up, the amount of polymer deposited has a linear dependence with pH so that the more acidic the polymer (higher doping level), the lower the amount of deposited polymer (after forming a relatively uniform first layer on the glass substrate). Another important feature observed is that each POEA/CnF bilayer contributed to an approximately equal amount of deposited material, indicated by the correlation of the straight lines (R^2>0.97) in Fig.1, which imply that regular multilayers were obtained. The ratios between slopes (n) of these lines give an idea of how efficient alternate adsorption of POEA/CnF is compared to multi-immersions of POEA. The values of n for pH 2, 3, 4 and 5 were, respectively, 4.9±1.4, 1.2±0.2, 2.0±0.3 and 0.9±0.2, which show that the amount of POEA deposited when alternated with CnF can be as high as 4.9 times the amount of multi-immersions of POEA, suggesting that it was possible not only to assemble alternate multilayered films of POEA and CnF, but also to control their thickness by controlling both pH and number of layers. AFM images of Fig. 2 clearly confirm the presence of CnF within POEA/CnF self-assembled films investigated. A globular morphology is obtained for plain POEA films, whereas a typical fibrillar morphology is observed for the films containing cellulose nanofibrils.

These results confirm that multilayered thin-films of POEA and CnF could be successfully produced at different pH under the conditions investigated. Such nanostructured composites might find interesting applications such as in sensors, biomedical materials and electronic displays.



(a) (b)

Figure 1: a) amount of adsorbed material as a function of deposition time for 10^{-3}M POEA and **b)** POEA/CnF at pH 2, 3, 4 and 5.



(a) (b)

Figure 2: 3D AFM images of self-assembled thin films showing the top layer (10th immersion of POEA or 10th bilayer of POEA/CnF) of POEA **a)**, and POEA/CnF **b).**

References

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