Experimental Report

Proposal: **9-12-333** **Council:** 10/2012

Title: Investigation of the architecture of new cellulose nanocrystals/polymer multilayers

This proposal is resubmission of: 9-12-314

Researh Area: Soft condensed matter

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Local Contact: WATKINS Erik

Samples: cellulose, poly-l-lysine, lignin, poly allylamine, hemicellulose

Instrument	Req. Days	All. Days	From	To
FIGARO	2	2	05/06/2013	07/06/2013

Abstract:

Cellulose nanocrystals (CNCs) are crystalline rodlike nanoparticles that are highly attractive candidates for the preparation of high-performance biobased materials. The layer-by-layer assembly was thus used to build thin nanocomposite films consisting of multiple layers alternating CNCs and polymer chains, which exhibit interesting mechanical or optical properties. The proposed experiment aims at the detailed characterization of the out of plane structure of various new CNCs/polymer films using neutron reflectivity. The structure of the films will be tuned by varying different parameters, namely the geometry and aspect ratio of the CNCs using two different cellulose sources, the nature and strength of the CNCs-polymer interaction (e.g. electrostatic or non-electrostatic) and the number of CNCs/polymer bilayers. This strategy should lead to unseen architectures that will alow us to broaden the physical properties and applications of the films. This study will benefit from the intracrystalline deuteration and from the high momentum tranfer range provided by the high flux ILL reactor.

Experimental report

Experiment number 9-12-333
Figaro instrument, June 5-6 2013

Local contact : Erik Watkins
Users : Clélia Martin, Laurent Heux and Bruno Jean

Introduction

This research project deals with innovative hybrid cellulose nanocrystals (CNC)/Gibbsite platelets (GW) multilayered films. To the best of our knowledge, our work constitutes the first time that cellulose nanoparticles have been associated with mineral platelets in multilayered films. This novel system may display exceptional mechanical properties thanks to the very high Young modulus of both components and also optical properties like antireflection thanks to a highly tunable architecture of the films.

Goal of the experiment

The growth of multilayers composed of CNCs and GW has been studied by atomic force microscopy up to 15 bilayers. We could reveal with this technique that both the presence of a drying step between each deposition step and the ionic strength of the CNC suspension had a very strong influence on the final thickness, e.g the growth being twice more rapid without intermediate drying. The purpose of the experiment was therefore to elucidate these phenomena and obtain the detailed internal structure of the films built under various experimental conditions.

Method

We measured the reflectivity at the air/solid interface of 4 (GW/CNC) multilayered systems with increasing number of bilayers, *m*, and made with different physicochemical parameters that influence the internal film's architecture. Both hydrogenated CNC (h-CNC) and deuterated CNC (d-CNC) were used.

(GW/h-CNC 0 mM NaCl)$_{m=1,2,3,4,7}$ made with intermediate and final drying steps
(GW/h-CNC 0 mM NaCl)$_{m=2,4,7}$ made only with a final drying step
(GW/d-CNC 10 mM NaCl)$_{m=1,2,3,4,7}$ made with intermediate and final drying steps
(GW/d-CNC 10 mM NaCl)$_{m=2,4,7}$ made only with a final drying step

The reflectivity spectra of all samples were measured in the time of flight mode for two different incident angles (0.624° & 3°) to cover a q-range equal to $8*10^{-3}$ to $3*10^{-1}$. All the spectra were fitted with Motofit software. A higher resolution (2%) but a smaller q-range were used for the thickest samples.

Results

Figure 1 shows the reflectivity curves of (GW/deuterated-CNC10mMNaCl)$_m$ multilayers made with intermediate and final drying steps for m=1 to 7. In order to have a better insight on the first oscillations and their evolution with increasing m values, the spectra were shifted from one another on the RQ^4 axis and the Q range was reduced.

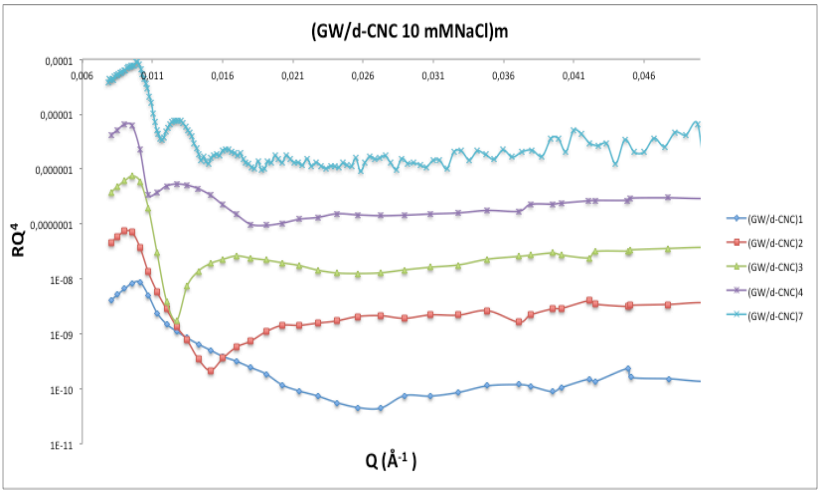

Figure 1. Neutron reflectivity curves of multilayer samples (PEI/PSS/PAH/PSS)/(GW/d-CNC10mMNaCl)$_m$ with m= 1, 2, 3, 4 & 7 built using intermediate and final drying steps.

Kiessig fringes in Figure 1 shift to lower Q values when m increases, inferring an increase in the total film thickness with increasing number of layers. No bragg peak can be distinguished, suggesting that the structure is not as stratified as was the case of polymer/CNC multilayers (Jean *et al*. 2008, 2009). Oscillations tend to vanish rapidly reflecting very rough interfaces.
In the fitting procedure, because of the lack of stratification between the GW and the CNCs layers, it was not possible to make a model in which every created layer corresponds to a layer of either CNC or GW. Instead, one layer in the model corresponds to one bilayer in the real film. We obtained the SLD profiles shown in Figure 2 from the fitting data analysis procedure.

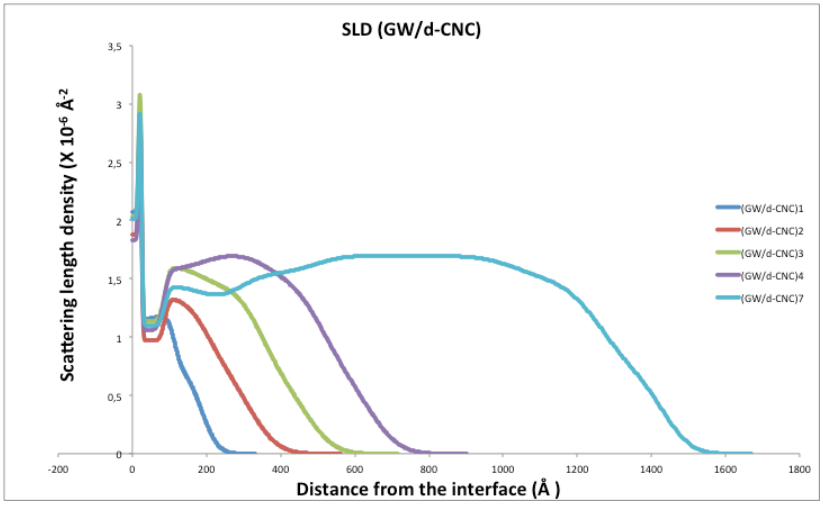

Figure 2. SLD profiles of multilayer samples (PEI/PSS/PAH/PSS)/ $(GW/d\text{-}CNC10mMNaCl)_m$ with m= 1, 2, 3, 4 & 7 built using intermediate and final drying step

The SLD is rather constant with the number of bilayers, which suggests that the nanoparticles density is the same when the film gets thicker. To be able to determine the particles volume fraction of each constituents, we must complete these data by measuring the complementary system *i.e*. (GW/hydrogenated CNC 10mM NaCl) made with intermediate and final drying steps (planned in June 2014). However, we could extract the thickness of each bilayer and the total film thickness that was compared with results measured by AFM scratch analysis (Figure 3). A very good agreement between the two techniques is observed.

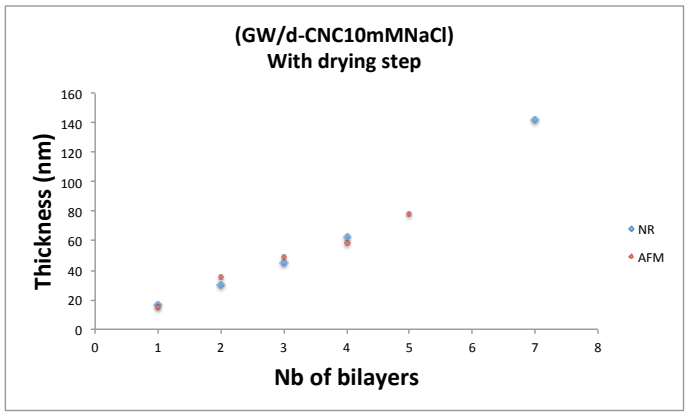

Figure 3. Thickness *versus* number of bilayers of (PEI/PSS/PAH/PSS)/ $(GW/d\text{-}CNC10mMNaCl)_m$ with m= 1, 2, 3, 4 & 7 built using intermediate and final drying step. Comparison between AFM and NR measurements.

The SLD profiles obtained for the multilayered system : (PEI/PSS/PAH/PSS)/ $(GW/h\text{-}CNC0mMNaCl)_m$ with m= 1, 2, 3, 4 & 7 built using intermediate and final drying step is plotted in Figure 4. Compared to the previous system (ie (GW/d-CNC 10 mMNaCl) made with intermediate drying step), the SLD seems to decrease with the number of bilayers. This infers a decrease in the particles density with increasing number of bilayers

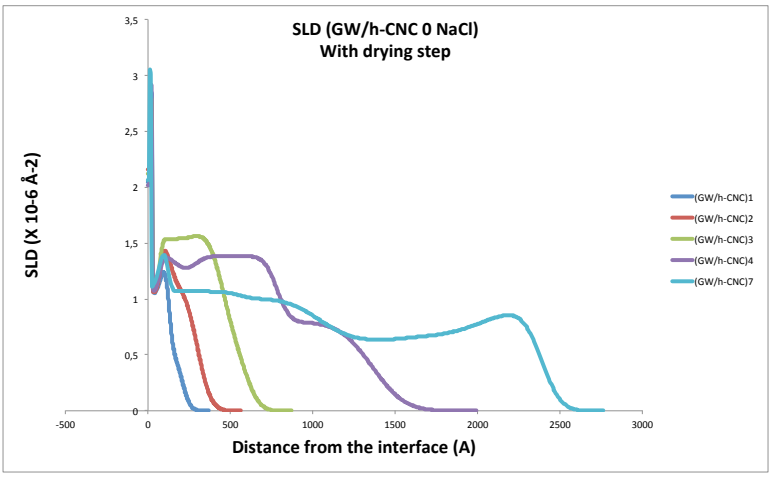

Figure 4. SLD profiles of multilayer samples (PEI/PSS/PAH/PSS)/ (GW/h-CNC0mMNaCl)$_m$ with m= 1, 2, 3, 4 & 7 built using intermediate and final drying steps.

Figure 5 shows a good agreement between the total film thicknesses measured by NR and by AFM.

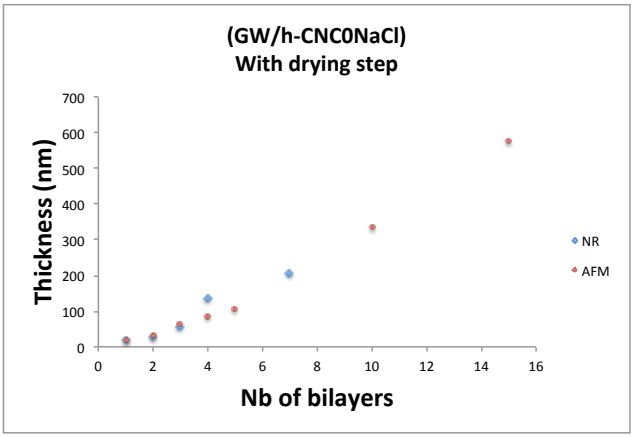

Figure 5. Thickness *versus* number of bilayers of (PEI/PSS/PAH/PSS)/ (GW/h-CNC0mMNaCl)$_m$ with m= 1, 2, 3, 4 & 7 built using intermediate and final drying steps. Comparison between AFM and NR measurements.

The same data analysis was performed for the two other systems ie :
(GW/d-CNC 0mMNaCl)$_{m=2,4,7}$ made only with a final drying step
(GW/h-CNC 10mMNaCl)$_{m=2,4,7}$ made only with a final drying step

Conclusion

Neutron reflectivity was successfully performed on multilayered thins film composed of cellulose nanocrystals and gibbsite platelets. By applying an intermediate drying step or by changing the ionic strength of the CNC suspension, the internal architecture can be tuned leading to 4 different architectures. The measurements performed gave us the total film thickness, the thickness and roughness of each bilayer. The obtained SLD profiles enable us to see if a decrease in the nanoparticles density occurs while the multilayers get thicker. However, to quantitatively measure the nanoparticles volume fraction, we need to perform new measurement on the complementary systems. Thus, NR appears essential to fully characterize the inner structure of (GW/CNC) multilayers.