Experimental Report

16/09/2014

Proposal: **9-12-350** **Council:** 4/2014

Title: Swelling properties of hybrid (cellulose nanocrystals/Gibbsite platelets) multilayered films

This proposal is a new proposal

Researh Area: Soft condensed matter

Main proposer: **JEAN Bruno**

Experimental Team: MARTIN Clélia
JEAN Bruno

Local Contact: BARKER Robert

Samples: cellulose

Instrument	Req. Days	All. Days	From	To
FIGARO	3	3	23/09/2014	26/09/2014

Abstract:

In the framework of the PhD thesis of Clélia Martin (ILL-CERMAV), we are investigating innovative hybrid organic/inorganic multilayered films comprising alternated layers of cellulose nanocrystals (CNCs) and Gibbsite platelets (GW). CNCs are rod like biosourced nanoparticles exhibiting outstanding physical properties that appear as perfect building blocks for the preparation of green or hybrid nanocomposites. The association of CNCs with Gibbsite (AlOH3) hexagonal nanoplatelets in thin films built using the Layer-by-Layer assembly technique constitutes a real challenge for the building free-standing films and coatings with enhanced mechanical and barrier properties. The architecture of (CNC/GW) multilayered films was shown to be highly tunable by varying the drying protocol and the salt content. We propose here to investigate by neutron refelctivity the swelling properties of (GW/CNC) multilayers. It indeed appears crucial to check if phenomena like swelling, thickness increase, rearrangement of the nanoparticles, or desorption occur. This study will benefit from the intracrystalline deuteration and from the high momentum tranfer range provided by the high flux ILL reactor.

Experiment number 9-12-333

Introduction

This research project deals with cellulose nanocrystals (CNCs) in multilayered films and aims at establishing the relationships between the internal structure of the multilayers and their mechanical and/or optical properties. CNCs are renewable rod-shape nanoparticles produced by the sulfuric acid hydrolisis of cellulose fibers. Their outstanding physical properties (E=150 GPa) made them perfect building blocks for the elaboration of green nanocomposites. Since CNCs possess negative sulfate esters at their surface, they can be associated to positively charged polyelectrolytes into multilayered thin films by using the famous *layer-by-layer* technique. In this conext, we decided to investigated an innovative hybrid system made of CNCs and another hexagonal nanoparticle named Gibbsite.

Method

We measured the reflectivity at the air/solid interface of 4 (GW/CNC) multilayered systems with increasing number of bilayers and made with different chemicophysical parameters that influence the internal film's architecture :

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

The reflectivity spectra of all samples were performed 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.

Results

Figure 1 shows the reflectivity curves of (GW/deuterated-CNC10mMNaCl)m multilayers made with intermediate and final drying step 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.

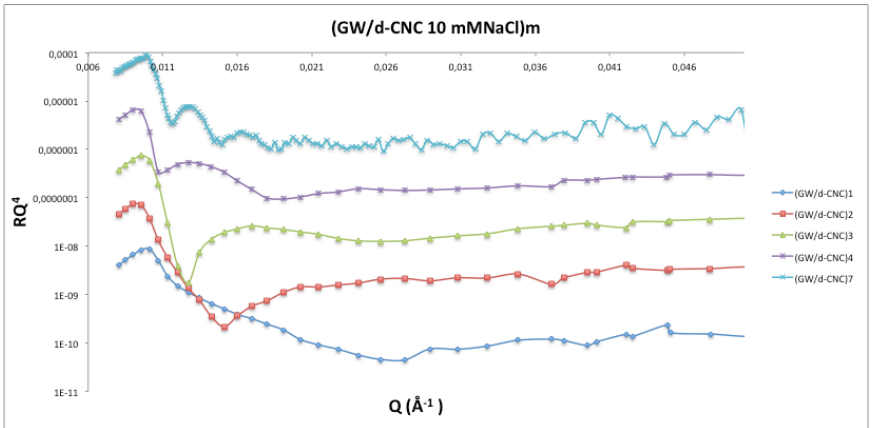

Figure 1. Neutron reflectivity curves of multilayer samples (PEI/PSS/PAH/PSS)/ (GW/d-CNC10mMNaCl)$_m$ with m= 1, 2, 3, 4 & 7 built using intermediate and final drying step

Kiessig fringes in *Figure 1* shift to lower Q values when the film grows, inferring an increase in the total film thickness. No bragg peak can be distinguish, which means that the structure is not as stratified as it could be for polyelectrolyte/CNC multilayers (B. Jean *et al. Langmuir* 2008). 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 correspond to a layer of either CNC or GW. Instead, one layer in the model corresponds to one bilayer in the real film. We obtain the following SLD profiles as a function of the distance from the Si interface.

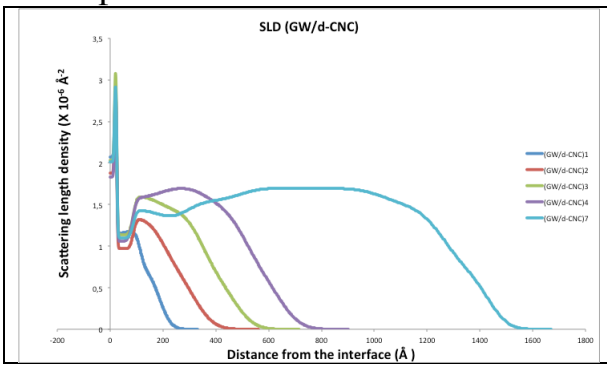

Figure 2. SLD profiles of multilayer samples (PEI/PSS/PAH/PSS)/ $(GW/d\text{-}CNC10mMNaCl)_m$ with m= 1, 2, 3, 4 & 7 built using intermediate and final drying step

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 this data by measuring the complementary system ie (GW/hydrogenated CNC 10mM NaCl) made with intermediate and final drying step (planned in June 2014). However, we could extract the thickness of each bilayers and the total film thickness that was compared in the *Figure 3* to previous results measured by AFM scratch analysis. We see a perfect agreement between the two techniques

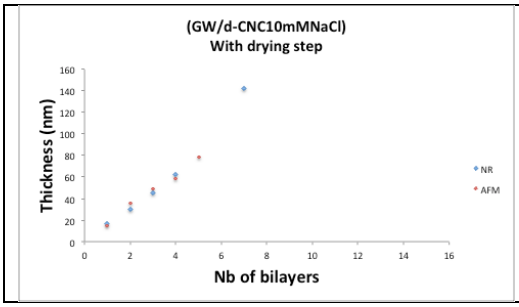

Figure 3. Thickness *versus* number of bilayers of (PEI/PSS/PAH/PSS)/ $(GW/d\text{-}CNC10mMNaCl)_m$ with m= 1, 2, 3, 4 & 7 built using intermediate and final drying step. Comparison between AFM and NR measurements.

Similar resluts were obtain for the three other systems ie :
$(GW/CNC\ 0mMNaCl)_{m=2,4,7}$ made only with a final drying step
$(GW/CNC\ 10mMNaCl)_{m=1,2,3,4,7}$ made with intermediate and final drying step
$(GW/CNC\ 10mMNaCl)_{m=2,4,7}$ made only with a final drying step