# Preparation and study of food packaging composites based on nano-lignocellulose and PVA/Chitosan

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## Introduction

The global demand on utilizing sustainable and ecologically friendly products based on raw materials has as result intense research on potential application of cellulose materials. Cellulose Nano-Fibrils (CNF), Nano-Crystalline Cellulose (NCC), purified or as lignocellulose, and bacterial nanocellulose (BNC) are intended to the development and application of high-performance industrial nanocomposites. Especially for lignocelluloses, the less energy/time consuming processes required to turn the biomass into the final nanostructured filler and the presence of lignin, which may be helpful for some applications, are key-factors that render these materials scientifically attractive.

Due to the fact that the use of plant waste could prove to be a useful but also environmentally friendly process, in the context of the HIPERION project, different types of nanolignocelluloses and bacterial nanocelluloses are being prepared. These cellulose-based materials are being incorporated into polymer/biodegradable matrices, aiming to enhance the barrier efficiency of the nanocomposites and modify their mechanical properties towards the generation of new food packaging materials with minimum environmental impact.

The present work focuses on the development and study of food packaging composites by using the water soluble Polyvinyl Alcohol (PVA) and/or the biodegradable Chitosan as polymeric matrices[1,2].

## Materials and Methods

Both PVA and Chitosan films are produced at lab scale by film casting from aqueous solutions, while the different types of cellulose (NCC, nano-fibril lignocellulose and BNC) are dispersed in triple distilled water (TDW) before being mixed with the polymeric solutions. In the case of chitosan, a further treatment process is applied in order to remove excess and bound acetic acid, which is needed to dissolve chitosan in aqueous solutions (0.5% v/v). For this reason, the chitosan nanocomposites are being immersed for several minutes in 1M NaOH aqueous solution, and then rinsed with TDW.

The structure of the cellulose samples as well as that of the polymeric matrices used, as well as the composites prepared, have been extensively studied at the molecular scale. The molecular characterization is carried out by using Raman and FTIR spectroscopy, while the morphological and crystallographic study is carried out by Scanning Electron Microscopy (SEM) and X-ray diffraction (XRD). Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Analysis (DMA) are used to determine the thermal properties of the composites such as the melting point and glass transition, respectively. Any change may lead to conclusions about the polymeric chain re-arrangement after the preparation processes and cellulose incorporation. Finally, due to EU regulations for food packaging, all of nanocomposites are being tested for migration control, using UV-Vis and/or Surface Enhanced Raman Spectroscopy (SERS) for the evaluation of migration of molecular species into food simulants.

## Results and Discussion

Structural characterization of all samples (from pristine to final composites) highlights the molecular and crystallographic changes that take place on the samples, after various cellulose loadings. The 3D nano-fibrous network (diam. of up to 50nm) of the produced lignocellulose from hardwood wastes, has been illustrated through SEM (Figure 1, left). Details associated with the monitoring of the lignin concentration in lignocelluloses obtained from hardwood and softwood are revealed by FTIR spectroscopy (Fig.1 on the right). To this end the relative intensity of the ring stretching vibrations (at e.g. 1509 cm$^{-1}$) of the lignin component with respect to the intensity of the cellulose ether band at ~1050 cm$^{-1}$ characterizes the specific type of lignocellulose.
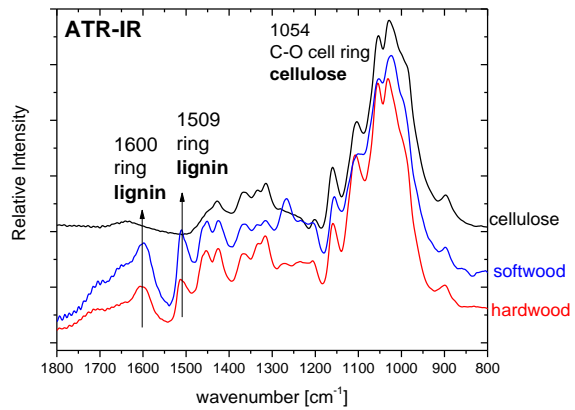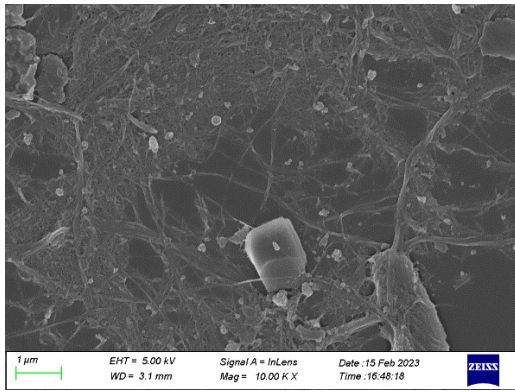
**Figure 1.** SEM image showing the morphology of hardwood-waste lignocellulose (left) and molecular characterization of cellulose samples by ATR/FTIR (right).

Crystallographic changes of the polymer/cellulose blends are extensively studied by XRD and the relevant thermal properties by DSC. Some comparative results of PVA-CNC composites are shown in Figure 2.
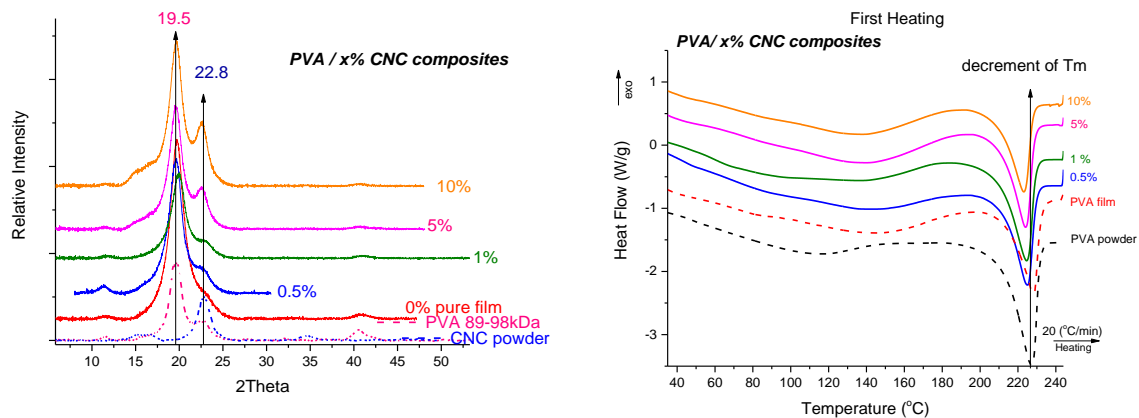


**Figure 2**. Characterization of PVA nanocomposites for various CNC loadings: XRD (left) and DSC (right).

The presence of cellulose is verified (22.8º peak) by XRD (Fig. 2 left) and the loading in the composites can be monitored via the cellulose 22.8º peak intensity (in respect to PVA 19.5º ).Furthermore, PVA % crystallinity can be extracted only after fitting the XRD line profiles with two peaks: one attributed to the amorphous halo (centre ~20º) and the 19.5º peak, associated with crystalline PVA. From the DSC thermograms (Fig. 2 right) it is found that the melting point of the polymer matrix decreases as a function of loading, while its (%) crystallinity exhibits a maximum at ~1% cellulose loading.

Similar results are also obtained for Chitosan or PVA nanocomposites with different kind of celluloses (CNC, lignocellulose, BNC).

Finally, taking into account the EU regulations for food packaging materials, the prepared composites are being tested by using accredited migration cells. Aqueous ethanol solutions are used as food simulants and the migration of molecular species and/or nanoparticles from the composites are being tested for a period of 1-30 days using UV-Vis and / or Surface Enhanced Raman Spectroscopy (SERS).

**Conclusions**

In conclusion, polymeric films of PVA and/or Chitosan and their composites with nano cellulose and nano lignocelluloses of various origins, have been prepared, thoroughly characterized by several techniques and tested under EU regulations for plastic materials and articles intended to come into contact with food.

**References**

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