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PLA based nanocomposites with Cellulosic and Lignocellulosic nanofibers as a biodegradable solution for green food packaging

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Abstract. The HIPERION project aims at the sustainable production of various types of nanocellulose, such as microfibrillated cellulose (MFC), cellulose nano-fibrils (CNF), nanocrystalline cellulose (NCC) and bacterial nanocellulose (BNC), for the development of high-performance industrial materials for green food packaging, paper packaging, adhesives and wood coatings.

In that manner, different types of cellulosic and lignocellulosic fibers (i.e., CNF and LCNF received from University of Maine and API-Europe respectively), after freeze drying at -50 ºC, were incorporated to PLA (grade 3052d from NatureWorks) by melt blending at various concentrations with or without the incorporation of the crosslinking agent Dicumyl Peroxide (1% or 3% wt.). The final films were produced after melt pressing. Thermal treatment on samples containing the peroxide initiator has been shown to crosslink PLA and also graft chains to cellulosic fibers (Wei et al., 2016).

The chemical composition and structure of the produced films were studied via Raman spectroscopy (μRaman T-64000), IR transmission (FTIR/IR) and Reflectance (ATR/IR) measurements (Bruker Alpha II), while their thermal and thermomechanical properties were studied by Differential Scanning Calorimetry (DSC Q100) and Dynamic Mechanical Analysis (DMA 850).

The suitability of the final products is performed by a release study of different molecular entities migrating through the polymer matrices in EU certified food simulants, using certified methodologies (i.e., UV/VIS, Surface Enhanced Raman Spectroscopy SERS, etc.) and specially designed cells/devices.

Keywords: Bioplastics, Food Packaging, Lignin, Nanocellulose, Nanofibers

1. Introduction

In recent global pollution crisis, various biodegradable and compostable polymers (Polylactic Acid, PolyHydroxy Alkanoates, PolyCaprolactone etc.) provide an excellent solution towards a sustainable future. Produced from renewable feedstock, these materials are nowadays selected as green and eco-friendly food packaging materials. Their properties however (thermal, mechanical, chemical resistance, etc.) require modifications.

Cellulosic and Lignocellulosic nanofibers are considered a green alternative to common synthetic fibers as low cost additives, improving the degradability and minimizing the toxicity. Their contrasting hydrophobic and hydrophilic nature in accordance, poses the greatest challenge for commercial use and green food packaging (Hemmati et al., 2021). In fact, the grafting of PLA chains onto these biofibers can improve the inherent difficulties and provide new opportunities for applications (Dhar et al., 2016).

2. Results

2.1. Spectroscopic Characterization of films based on the novel bioplastic formulations.

Firstly, the films produced after melt blending of various types of freeze-dried nanocellulose at different concentrations with PLA were evaluated regarding their FTIR vibrational spectra. Compared to the spectra of pristine PLA, a broad doublet peak at 3400 – 3100 cm^{-1} is characteristic of hydroxyl stretching vibration v_s(OH) of cellulose in all cellulose containing films as depicted in **fig.1**. In presence of the crosslinking agent however, decomposition remnants (i.e., acetophenone) can also be identified in the IR spectra by the presence of peaks at 1690 and 1600 cm^{-1}. These entities when in contact with foodstuff can alter taste and odour which are undesirable for food packaging purposes. Due to their volatility these by-products, during a typical for PLA thermal annealing, escape the matrix which then remains purified and preferable to use. Collectively, these vibrational band assignments mentioned for the different chemical entities are listed in **table 1**.

Table 1. FTIR absorption bands of the different chemical entities present in the final films. (Marrucho et al., 2022) (Yang et al., 2007)

v (cm^{-1})	Vibrational Band Assignments
3700-3450	vOH (PLA)
3400-3100	vOH (Cellulose)
3000-2800	vCH_3 (PLA)
1690	C=O (Acetophenone)
1600	Ring vC-C (Acetophenone)
960, 925 (CR)	rCH_3+vCC (PLA)
875	vC-COO (PLA)
800-600	γC-O (PLA)
561	vC-C (Cellulose)

2.2. Thermal and Thermomechanical analysis.

Thermal analysis via DSC as shown in **figure 2 (left),** displays the effective crosslinking or grafting of the nanofibrils onto the polymer backbone, as the melting point depression for crystals formed with the same supercooling degree is analogue to tacticity and defects/branches introduced. Alongside the initial D-Lactic acid effect due to its initial random introduction to the backbone, a supplementary melting point drop is observed due to the integrated concentration of the crosslinker. However, the inherent minimal interaction of cellulose-based nanofibers with the polymer matrix is understood as no melting temperature difference is visible in the PLA/CNF blends. Isochronal dynamic mechanical **(right)** analysis shows not only the melting temperature drop but also the extended toughness of all Semicrystalline materials above the Glass transition.

A release study was implemented afterwards to evaluate the performance and suitability of these films as bioplastic food packaging. The specimens were left 10 days in contact with EU Regulated food simulants, namely Simulant A, C and D1 consisting of 10%, 20% and 50% $EtOH/H_2O$ respectively. No crosslinking byproduct migration was observed in the food simulants proving the capability of these novel materials as greener food packaging alternatives.

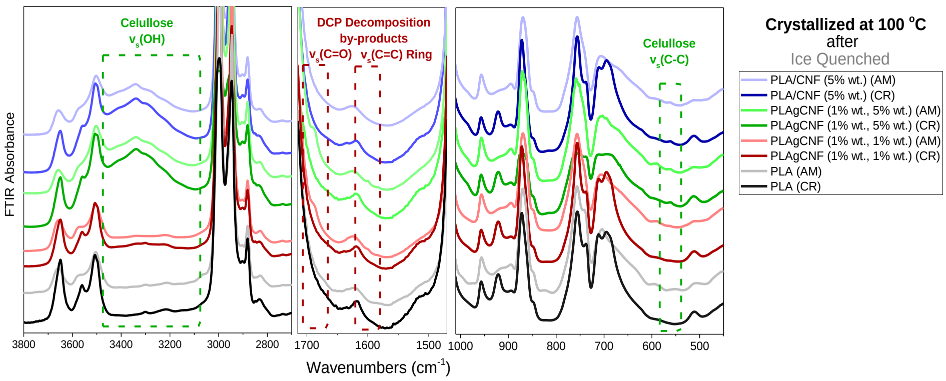

Figure 1. Effect FTIR transmission spectra of PLAgCNF and PLA/CNF films after ice quenching (AM) and further thermal annealing at 100 ºC.

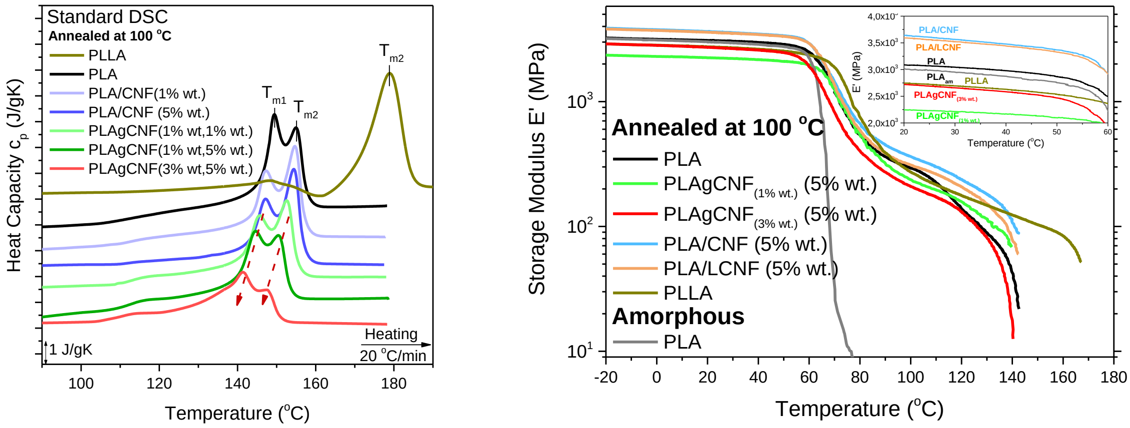

Figure 2. (Left) DSC and **(Right)** Isochronal DMA thermographs of PLA w/ and w/out the inclusion of various cellulose based nanofibers and the crosslinking agent.

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3. Conclusions

A series of novel green bioplastic formulations were developed for the purpose of reducing waste in food packaging applications. These materials were characterized spectroscopically in order to observe the formulating reactions and displayed adequate thermal and mechanical capabilities for this type of use. Lastly, EU regulated migration studies provided the last successful evaluation by testing contact with foodstuff with no release of processing byproducts.

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