

## Introduction

The last decade, awareness of climate change and depletion of fossil fuels has motivated the scientific community to search for sustainable alternatives to the conventional polymers.

One of these alternatives is lignin, a constituent of wood, holding the cellulose fibres and the hemicellulose together. As a by-product of paper and pulp industries, lignin is an inexpensive and abundantly available biopolymer.

This makes lignin an attractive biomaterial, and it has already been studied for many different applications, e.g. as flame retardant, as antioxidant, as polymer filler or as feedstock for the production of carbon fibres.

In this article, the potential of lignin for the production of porous carbon fibres will be described. Porous carbon fibres are used in non-structural applications, e.g. filtration or electrochemical processes, such as energy storage platforms for cars and aircrafts.

Among the precursor fibres used in the production of carbon fibers, polyacrylonitrile (PAN)-based ones are most popular. Being a biobased, inexpensive and easily available waste material, lignin has a large potential to replace this fossil-based PAN as a carbon fiber precursor.

However, processing of lignin is technically challenging. Extensive cross-linking and strong intra-molecular interactions constrain its processing window. To overcome these issues and obtain more desirable properties, polymer blending is a very convenient method.

Within the H2020 LIBRE project, continuous fibers are produced based on lignin through careful polymer selection and control of the processing conditions.

## Material description

For processing, lignin with a thermoplastic behaviour is required. The selected lignin is a modified hardwood type. To evaluate the thermal behaviour, DSC and TGA measurements were carried out on undried samples with a water content of 3%.

A heat-cool-heat run was performed with heating and cooling rates of 10 degrees per minute. The cooling curve shows no crystallization peaks, which is an indication of the amorphous nature of lignin. From the second heating curve, a  $T_g$  of 109° can be derived.

Thermal stability was investigated using thermogravimetric analysis (TGA). This was done in a nitrogen atmosphere with a heating rate of 10° per minute. Between 1% and 5% weight loss, the temperature goes from 229° to 277°. The melt flow index at 200° is approximately 3.8 g/10 min.

Blends are produced by mixing lignin with polylactic acid or PLA, a thermoplastic polymer derived from renewable resources like corn starch or sugar cane.

The tested PLA grades are 6400D (produced by NatureWorks) and L130 (produced by Corbion). PLA 6400D has a  $T_g$  of 60° and a melting temperature ( $T_m$ ) of 168°. The melt flow index at 210° is 6 g/10 min. The PLA L130 grade has a similar  $T_g$  and a  $T_m$  of 175°. Its melt flow index is 16 g/10 min at 210°. Both grades are thermally stable up to 300° and higher.

Next to blends composed solely of lignin and PLA, blends composed of lignin, PLA and polyethylene glycol (PEG,  $M_w$  8000) were also tested. In literature can be found that PEG can act as a plasticizer for lignin. As both lignin and PLA are rather brittle materials, the use of PEG could assist in improving the processability.

## Production of lignin blends

Prior to processing, the PLA granulates, and the lignin powder were dried in a vacuum oven at 80°, to avoid hydrolysis during extrusion. To obtain sufficiently high carbon yields, a lignin content of minimum 50% was chosen.

Blending of the materials was performed on a semi-industrial twin-screw compounder at 190°. The resulting extrudates are pelletized after cooling in a water bath.

The properties of the produced blends were characterized via DSC and TGA analysis. The glass transition temperature of all blends was remains close to 60°C. The melting point of the PLA L130 blend is a bit higher than for the PLA 6400D blends, see table. Based on TGA measurements, carbon yields (CY) between 20 and 24% can be obtained.

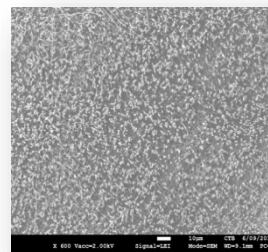
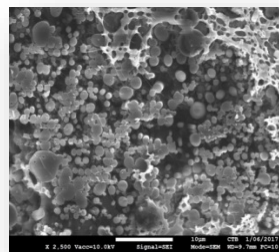
	$T_m$ (°C)	CY (%)
50/50 Lignin/6400D	156-165	23,7
50/45/5 Lignin/6400D/PEG	157-166	20,9
50/45/5 Lignin/L130/PEG	171	22,2

### Production of precursor fibres

All these blends were processed on a semi-industrial monofilament and multifilament extrusion line, using a temperature profile from 175° to 195°C. The blends without PEG are very brittle and could not be wound without breaking. Addition of 5% PEG improves the processability. The brittleness is reduced, allowing filament winding.



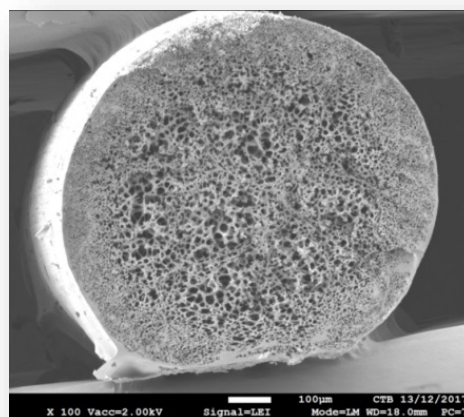
The SEM images present the cross-sections of the filaments. Figure 1 (blend without PEG) shows clearly the phase separation: PLA fibrils are formed within a lignin matrix. This indicates the low compatibility between the lignin and the PLA. In Figure 2 (blend with 5% PEG), the fibrils are smaller (below 1  $\mu\text{m}$ ), more uniform in size and more uniformly distributed within the matrix. This correlates with the improved processability. Further, the blend composed of PLA grade L130 is easier to process than the one made from PLA grade 6400D.



### Production of porous carbon fibres

Next step is the transformation of the best performing blend (i.e. 50% lignin, 50% PLA L130 and 5% PEG) into carbon fibres. This test was performed at lab-scale. The fiber was first stabilised in  $O_2$  to 250°, followed by carbonisation in  $N_2$  to 1000°.

The SEM image of the cross-section of the produced carbon fiber shows a porous structure caused by the phase separation between lignin and PLA. With further research and optimisation, these porous carbon fibres can be optimised for nanofiltration or energy storage applications, offering an alternative for complex and less sustainable methods such as electrospinning.





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