Functional Cellulose-Lignin-coating on Porous Materials

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Abstract

Utilising abundant bio-products in the industrial manufacturing process of various materials and products, is something that has been given elevated attention during the last few decades. Two such examples of bio-products are Cellulose Nano-Fibrils (CNF) and lignin. These two compounds are abundant in the sense that they can be produced from almost all tree-derived materials or other fibrous plant materials, they are low in toxicity, and they are environmentally friendly. In this work, we focus on utilising the bio-polymeric properties of CNF to create a coating on porous surfaces such as a piece of loosely woven cloth, and then using the CNF based coating as a platform onto which lignin can be sprayed, which have been chosen for its UV-protective properties.

This work proves that it is possible to create a CNF based coating, that lignin can be sprayed upon. The transmission properties of samples created with various parameters is presented, and it is concluded that, with further work, these components could be successful candidates for UV-protective coatings on porous materials.

Contents

1 Introduction

Cellulose-nano-fibrils (CNFs) and lignins are present in almost all fibrous plant materials on earth, meaning they are of an environmentally friendly nature, they have good bio-compatibility, and they are of low toxicity [1]. Cellulose-nano-fibrils are the most abundant bio-polymer in the world, and as such it can be produced en masse in major industries from bio-degradable materials. Recent developments in using CNFs as coatings have shown their use in various fields, ranging from super-hydrophobicity [5] to oleophobicity [4]. The challenges faced by groups trying to utilise CNFs have been linked to the expense of producing pure, bleached CNF in comparison to lignin-containing cellulose-nano-fibrils (LNCFs). While LNCFs are cheaper to produce, they have various effects on the final product as a result of what production method is utilised [3]. With these things taken into consideration, CNFs are of considerable interest. Lignins have been shown to be excellent candidates as UV-protective compounds due to chromophores present in the compound. However, their commercial use requires more research. In this work, the focus is on utilising CNFs to functionally coat cloth, which will then act as a platform onto which lignin can be deposited. Should this succeed, it could be an advancement in the UV-protective coating industry.

2 Materials

Hardware
Optical Microscope
J. A. Woollam M-2000 Ellipsometer
Spray Coater
Software
Julia Programming Language
J. A. Woollam CompleteEASE
Compounds
CNF 400 1:5 Water solution
Ethanol
Lignins

3 Methods

The methods that were utilised to conduct the experiments will be explained in detail in the following section. A piece of cloth is cut to an appropriate size of approximately 10x10cm. The cloth is then sprayed a distinct number of times, with various other parameters in a spray coater, which is explained below.

3.1 Solution preparation

The 1:5 CNF/water solution utilised in these experiments were prepared by another member of the group by use of centrifuge, and I had no hand in it.
One lignin solution was prepared. The solvent used was ethanol, and was produced in a fashion, which is described below:
The concentration of lignin is set to be 5.14 $\frac{g}{L}$, which is put into 10mL glass bottles containing the solvent. The glass bottles are sealed with parafilm and put into a sonication device for approximately 10 minutes, to ensure total dissolution of the lignin. The solution is then cleaned through 0.45μL filters.

3.2 Spray coating

The piece of cloth is laid in between two aluminium rings, the bottom one being of height $\approx$ 5cm. This is done to ensure that the piece of cloth that will become damp after it is sprayed, will not reach the platform it is placed on, and thereby lose CNF solution to the surroundings. The top ring acts as a funnel of diameter 7.0cm, giving a distinct area of spray on the cloth. The platform was heated so that the temperature of the environment was approximately 60°C. This was done to ensure that the CNF solution had time to dry after being sprayed onto the cloth. More details on these parameters and other parameters, such as spray time, waiting interval, and number of pulses, are discussed in section 4. The cleaning procedures for the spray nozzles are the following: When done with a spraying session, spray through a whole container of pure solvent, whichever solvent was used in the experiment.

3.3 Optical Microscopy

Optical microscopy was utilised to determine whether or not the CNF had properly coated the cloth, and also to investigate the amount of lignin which has been deposited onto the CNF coating, which can be seen on figures 3 and 6.

3.4 Spectroscopic Ellipsometry

Spectroscopic ellipsometry has been utilised to investigate the transmission properties and transmission profiles of the various coatings. The profile covers a wavelength range of $\approx 199nm - 1000nm$. The graphs resulting from these procedures can be seen in section 4.

4 Results and Discussion

The parameters that were ultimately decided upon during the spray coating process were a result of trial and error. The initial standard set of parameters for the CNF and lignin spray coatings were the following:

	Ethanol Lignin	CNF
Pulses	5	30 – 110
Spray Time	5	1.5 seconds
Wait Time	550 seconds	550 seconds
Temperature	112 °C	60 °C

Table 1: Initial standardised parameters of the various pulse regiments.

However, to provide a good background on which to hold the actual results, I will provide some of the data that led to the determination of these parameters. Initially, the samples were sprayed at room temperature, with a pulse duration of 1 second and a wait time of 600 seconds. The transmission profiles of these samples can be seen on figure 1, top. These can be compared to the more successful coatings and their transmission profiles shown in figure 1, bottom:

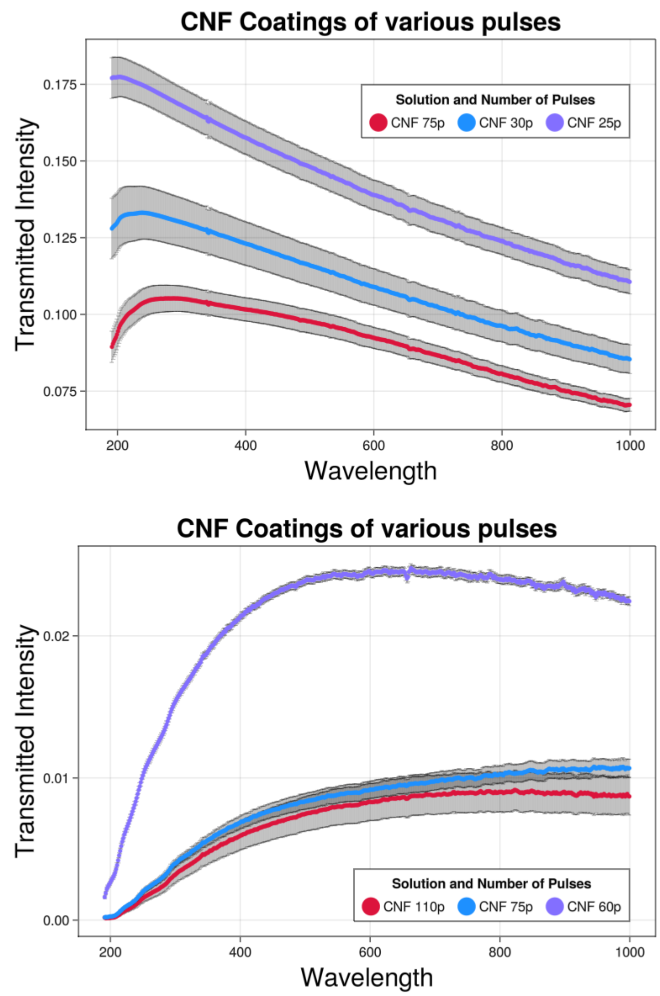

Figure 1: Top: Transmission Profiles from initial sample production of CNF coatings, where the coatings were not successful in covering the fabric and its pores. **Bottom**: Transmission profiles of fully formed, hole covering CNF coatings. Performed via spectroscopic ellipsometry, where the errors along the y-axis are the standard error of the mean.

4.1 CNF Coatings and Lignin Deposits

A note on the number of pulses used for spray coating various samples and the total amount of samples: Due to limited time available and inconsistent laboratory schedules, the range of pulses vary, indicated in table 1 and 2. The limited time at the spray coater, combined with the long production times, up to 16 hours, due to the samples having to dry, means that relatively few samples could be produced.

The CNF coatings and the successful parameters of the process has been explained in previous sections. The coating's weight was measured by measuring the weight of the sample before and after the coating had been applied, which can be seen on figure 4, left. As is always the case, the search for optimisation of the process is always ongoing. Referring to the bottom graph on figure 1, it can be seen that both 75- and 110 pulses were successful in completely coating the cloth, however, 60 pulses also has very agreeable characteristics, and it was therefore concluded that 60 pulses, at the initial specified standard parameters of table 1, were sufficient is providing an acceptable coating. Besides this, from figure 3, it can be seen that 110 pulses creates a thick coating, which is the not the aim of the CNF coating. It is simply to create a platform onto which lignin can be sprayed. Another point evident from these images, is that the CNF bio-polymer seems to have contractile properties, evident from the fact that the dimensions of the cloth pores seem to diminish as the CNF coating is produced. Setting 60 pulses as the standard, we moved on to spraying the solution of lignin onto the CNF coatings. Ethanol lignin was used on the graph on the bottom of figure 2. As can be seen on this graph, the transmission profile of the lignin-free CNF coating, lies in the middle of the region. As the lignin is sprayed onto the CNF coating, the transmission profile increases a significant amount, but as more lignin is deposited it falls again until 20 pulses of lignin, where it reaches beneath the initial CNF coating. This seems to suggest that the ethanol based solution could perhaps interfere with the CNF coating, until a significant enough lignin coating can become dominant. The interference behaviour cannot be seen on the 75 pulse CNF coating, on figure 2, bottom.

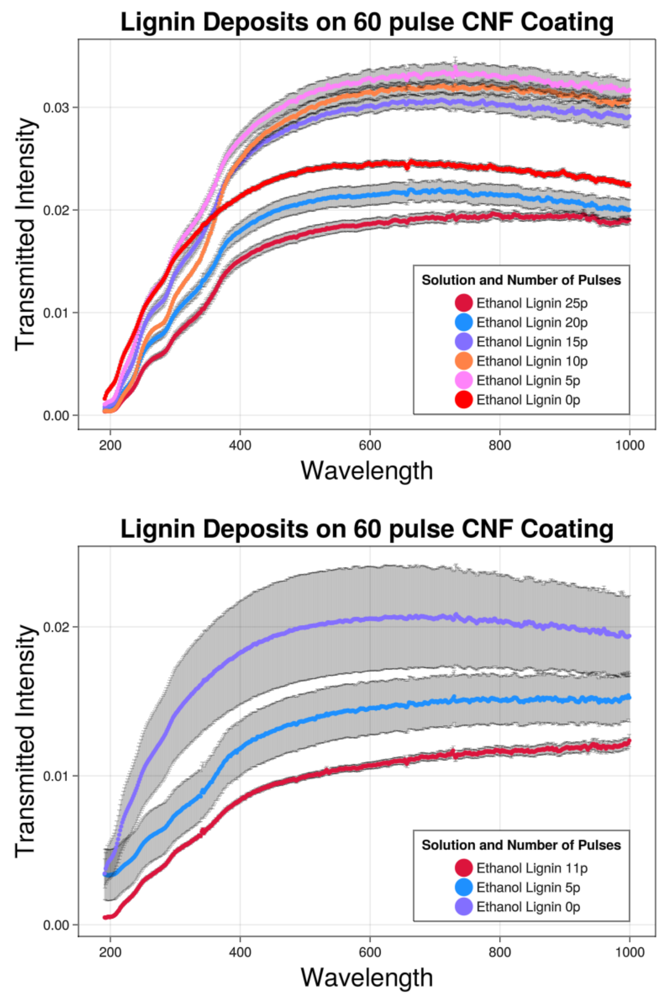

Figure 2: **Top**: The transmission profiles of various number of pulses of an ethanol based lignin solution, on a CNF based coating. The CNF coating is based on 60 pulses, where the parameters set can be seen in table 1. The error on the y-axis is the standard error of the mean. **Bottom**: Lignin pulses on 75 pulse CNF Coating.

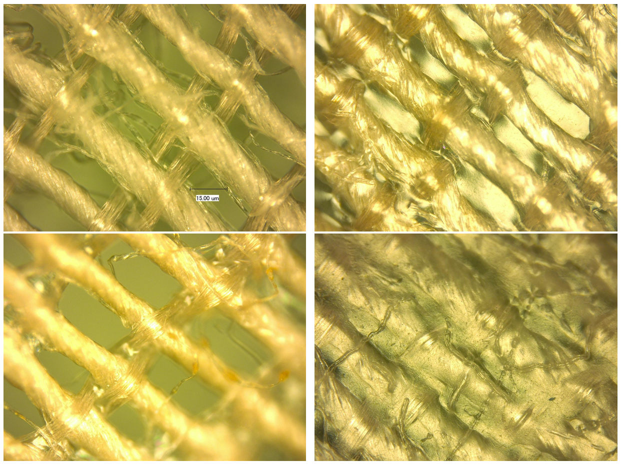

Figure 3: Top left: Image of untreated cloth and its pores. **Top right**: Image of CNF coating of 60 pulses, where 15 pulses of ethanol based lignin solution has been sprayed on top. **Bottom left**: Image of CNF coating of 60 pulses, outside of the region where a successful coating has been achieved, but where the region was still sprayed. This has been sprayed 15 times with an ethanol based lignin solution. A reddish colour is visible due to the lignin. **Bottom right**: Image of CNF coating of 110 pulses, where it can be seen that the coating is much thicker than the top right image.

The CNF coatings that have been produced via the described methods have a caveat in the fact that they are of a brittle structure and not very malleable. Methods that could be tried to help alleviate these issues, are described in section 5.

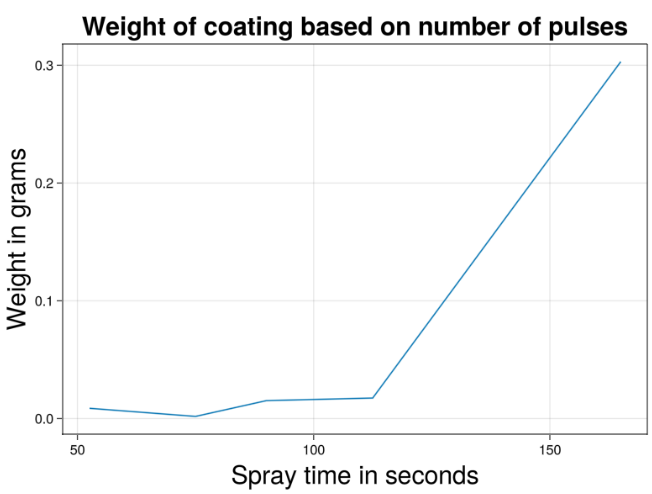

Figure 4: Weight of CNF coating as a function of total spray time in seconds.

were observed to run out after approximately 127.5 seconds of spray time. This may appear to be contradictory to the figure 4, but various other factors, such as temperature variations or the temperature of the CNF, as the supply was kept at approximately 5 °C, could explain the shape of the graph. Another factor could be the inconsistent pore size of the cloth. Most of the data presented in

Figure 5: Top left: Image of a 450 pulse CNF coating, with the parameters: 0.3 seconds spray time, 60 seconds between pulses, and a temperature of 60°C. It is secured in the holder used for ellipsometry measurements. **Top right**: Image of a 60 pulse CNF coating, utilising the parameters stated in table 1, which has also been treated with 25 pulses of ethanol lignin, also with parameters stated in table 1. The dashed, black circle indicates the area of effective CNF coating. It is approximately 0.5cm in radius. The dashed, black circle indicates the area that has been sprayed with lignin. **Bottom left**: Image of 450 pulse CNF coating, with the parameters as stated in the top left image. The dashed, red circle is the effectively CNF coated area. It is significantly larger than the sample made with the standard parameters. **Bottom right**: Image of a untreated sample and its dimensions.

this project has utilised the standard parameters outlined in table 1. However, towards the end of the project, these

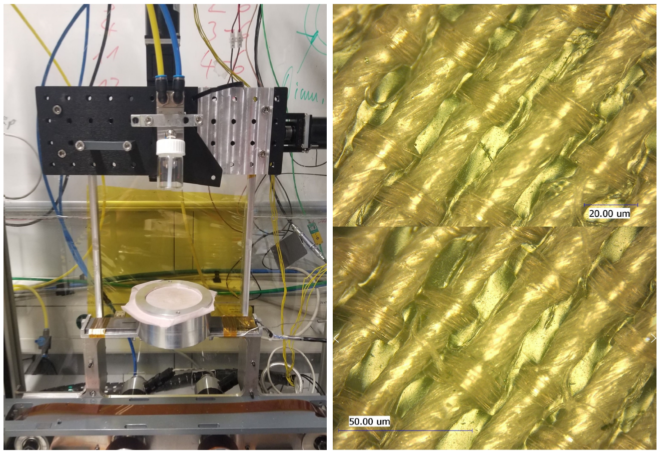

Figure 6: Left: Image of the experimental set-up in the spray coater, with a CNF container attached to the nozzle. Compressed air is in the yellow tube, and nitrogen in the blue. The holder and sample can be seen at the bottom. **Top right**: Image of a 450 pulse CNF based coating, with parameters: 0.3 seconds spray time, 60 seconds of wait time, and a temperature of 60°C. **Bottom right:** Image of a 450 pulse CNF based coating, of identical parameters as the image above.

parameters proved to be difficult for the spray nozzle to maintain, likely due to a build-up of CNF within the nozzle. The issue resulted in the spray coater not being able to run overnight, as it seemed to get completely blocked within 5-10 pulses. The nozzle was cleaned from this blockage by submerging the removable spraying head in acetone, putting it into the sonication device for 10 minutes, and then cleaning it with isopropanol. To combat the blockage, a new set of parameters were derived, which can be seen in table 2:

	Ethanol Lignin	**CNF**
Pulses	5	450
Spray Time	5	0.3 seconds
Wait Time	100 seconds	60 seconds
Temperature	112 °C	60 °C

Table 2: Second standardised spray parameters

These parameters were decided upon in the hope that much more frequent spraying, at shorter spray times, would result in the nozzle not becoming blocked, while maintaining the total amount of spray time in seconds as previous results. A look at the results of these parameters can be seen on figure 5, bottom left, and on figure 6, top and bottom right.

As can be seen on these figures, the second set of standardised parameters yielded a much larger effectively coated surface, which also seems to have a more spherical symmetry than the initial set of standard parameters.

Due to time constraints on the project, transmission measurements and lignin spraying could not be achieved on samples produced with the second set of standardised parameters. It is, however, recommended that the second set of parameters be the one that is continued to work with, should this work continue in the hands of others.

5 Future Work

5.1 Alleviating Issues with Current Procedure

To maintain manageable production times, it was concluded that the samples should be raised to 60°C during the CNF spraying. However, the raised temperature resulted in more brittle coatings. To produce flexible coatings, one method could be of a chemical nature. Either before the lignin spray, after, or both, give the cloth a methanol/ethanol/isopropanol bath. A combination of heating or cooling and a chemical bath could also be of interest.

Another method could be of a mechanical nature, insofar that the cloth could be "crumbled", to alleviate the brittleness of the coating. This could work for this specific purpose, as the coating does not need to be rigid or smooth. It only needs to cover the pores, so that lignin

can be sprayed on top of it.
The concentration of CNF in the CNF solution could be increased, to see if that could alleviate the need for elevated temperatures, as less water is needed for the same amount of CNF.

5.2 Ideas for New Procedures

The solvent used for the lignin can be interchanged for methanol, isopropanol, or other organic solvents to investigate if that could change the outcome, or the effectiveness of the lignin coating.
CNF 400 has been used throughout this project, as was suggested by advisor. The 400 is a measure of the amount of surface alteration the CNF has undergone, i.e., it is a measure of how much surface charge is available. The procedure can be changed to include higher or lower surface charge.
The use of LNCFs, as mentioned in section 1, could be included, as they seem a valid candidate for this specific project, as they are cheaper to produce and already include lignin.

6 Conclusion

From the work presented in this project, it can be concluded that it is possible to create CNF coatings on porous materials, such as pieces of cloth, and use these CNF coatings as bases for a lignin spray regime. The transmission profiles of the samples produced have shown that the motivation for the project has not been unfounded and that the CNF and lignin coatings produce transmission profiles similar to what has been expected. However, the process needs more investigation as the desired result is an indetectable coating, which we have not achieved. Various methods to alleviate the issues with the current method, such as chemical baths, changes in procedure, differing solvents, and temperature changes, have been suggested.

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