DEPARTAMENTO DE CIÊNCIA DOS MATERIAIS

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Licenciado em Engenharia de Micro e Nanotecnologias

Polymeric Functionalization of Recycling Newspaper

MESTRADO EM ENGENHARIA DE MICRO E NANOTECNOLOGIAS

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I leave you all with a smile on my face and a tear in my eye.

"Capa negra de saudade
No momento da partida
Segredos desta cidade
Levo comigo pra vida"

- Balada da Despedida, 5º Ano Jurídico, Coimbra

"You cannot teach a man anything; you can only help him discover it in himself."
(Galileo)

RESUMO

Nos últimos anos, tem havido uma preocupação crescente sobre o que fazer com os resíduos de papel. Tendo em vista essa preocupação surgiram maneiras criativas e interessantes de resolver esse problema. Uma delas é a reciclagem de resíduos de celulose empregada na mais avançada metrologia de papel de última geração. A estrutura básica da reciclagem dos resíduos de papel é reduzir a sua forma primária, ou seja, fibras de celulose, que são um bloco de construção para a fabricação de papel reciclado.

Neste trabalho, foi utilizado a polpa residual e esta foi refinada num método fácil e de baixo custo misturado com o polímero polipirrol para produzir papel eletrónico. Em seguida, foi criado um dispositivo de colheita de energia que funciona com base num sistema de transferência de cargas quando a força é aplicada na superfície do polímero. Este sistema tem como objetivo transformar energia mecânica em energia elétrica para alimentar o dispositivo.

Também foi determinado o papel que apresenta as melhores condições para formar este sistema.

No futuro, esta aplicação poderá ser usada para ajudar a desenvolver sistemas de colheita de energia que sejam pequenos e de baixo custo.

Palavras-chave: Resíduos de papel; Papel eletrónico; Reciclagem; Compósitos eletrónicos; Polipirrol; Colheita de energia;

ABSTRACT

In recent years, there has been growing concern about what to do with waste paper. In view of this concern, creative and interesting ways have emerged to solve this problem. One of them is the recycling of cellulose waste used in the most advanced state-of-the-art paper metrology. The basic structure of recycling waste paper is to reduce it to its primary form, i.e. cellulose fibers, which are a building block for the manufacture of recycled paper.

In this work, waste pulp was used and it was refined in an easy and low-cost method mixed with polypyrrole polymer to produce electronic paper. Next, an energy harvesting device was created, that works on the basis of a charge transfer system when force is applied to the polymer surface. This system aims to transform mechanical energy into electrical energy to power the device.

The paper that presents the best conditions to form this system was also determined.

In the future, this application could be used to help develop energy harvesting systems that are small and low-cost.

Keywords: Paper waste; Electronic paper; Recycling; Electronic composites; Polypyrrole; Energy harvesting;

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List of Abbreviations

AL – Active layer

APS – Ammonium persulfate

ATR – Attenuated Total Reflection

CA – Citric Acid

CCL – Charge Collective Layer

EDS – Energy Dispersive Spectroscopy

E-waste – Electronic Waste

FTIR – Fourier-Transform Infrared spectroscopy

PPy – Polypyrrole

SDS – Sodium dodecyl sulfate

SEM – Scanning Electronic Microscopy

WHO – World Health Organization

List of Symbols

***A* –** Area

g – Grams

***I* –** Current

***P* –** Porosity

***ρ* -** Density

***V* -** Volume / Voltage

1. INTRODUCTION

1.1. Context and motivation

Climate change is one of the biggest challenges that we face nowadays.

To fight this threat that affects all of Humankind, we need to find new ways to tackle this problem. One of the ways to reduce our impact on the environment and help fight Climate change is not only reducing and reusing, but also recycling the materials that we use daily. One of these materials is paper, which usually ends up in the Trash and which leads to dumps for disposal.

Besides the conventional applications, paper can be used in the field of electronics, having a lot of potential, deserving of attention and further research. However, there is still a lot of room for improvement not only in the area of paper electronics but also in new ways of recycling paper for more functional purposes.

The energy harvesting devices in this work is an extension of this area. The advantages provided by this device are: low-cost; flexible; uses waste for its composition.

1.2. State of the Art

In recent years there has been an increase in devices that are based in cellulose such as solar cells, energy storage and mechanical energy harvesters, sensors, etc...

The triboelectric nanogenerator (TENG) was first published in 2012 as a new form of technology for converting mechanical energy from the environment to electrical energy. [1] And ever since, there has been an increase in scientific literature.

. These charge transfer mechanisms is due to PPy being a conjugated conducting polymer.

1.3. Electronic Waste

In recent years there has been an increase in the production of electronic devices which has led to a growth in waste those results from these devices ending up in the trash without any kind of treatment nor action to recover the raw materials. These devices range from computers to mobile phones and many others. The world produces as much as 50 million tons of electronic and electrical waste a year (**Figure 1.1**). But only about 20% of this waste is recycled. [2]

The WHO (World Health Organization) Director-General, Dr. Tedros Adhanom Ghebreyesus, has also stated that we are facing a "tsunami of e-waste" [3]. E-waste will have a significant impact on our planet's and population's future.

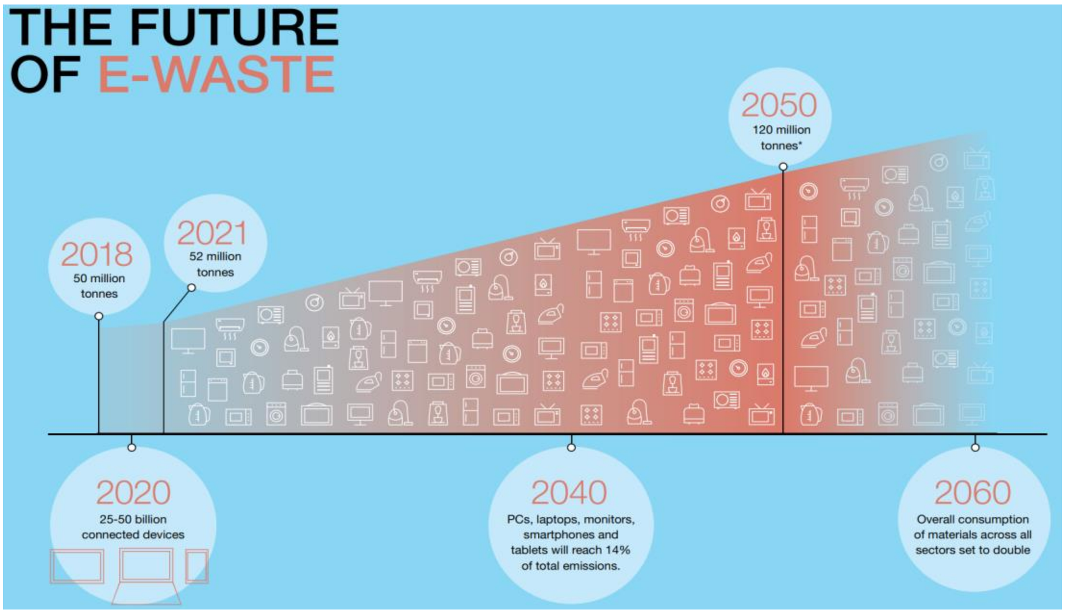

Figure 1.1 — Graphical Representation of the Evolution of E-waste from 2018 to 2060. Showing an increase from 50 million in 2018 to 120 million in 2050. [1]

1.4. Recycling Electronic Waste

Now that it is established that e-waste is a concern, recycling could be a good option to approach this problem.

Recently, a new study was published providing us some key insights into new ways to recycle e-waste paper and studies on the topic of e-waste paper (more specifically in China). In that study is highlighted that China has the highest production of e-waste (25.7%) compared to other countries. But also ranked first and published over 1300 peer-reviewed papers on e-waste since 2000 (**Figure 1.2**). [4] Also, recycling e-waste is more cost-effective than virgin mining. By recycling, we could save huge amounts of waste and still be able to extract materials from them. And the potential for the recycling of e-waste was expected to reach $73.4 billion US dollars by the year 2030. [4]

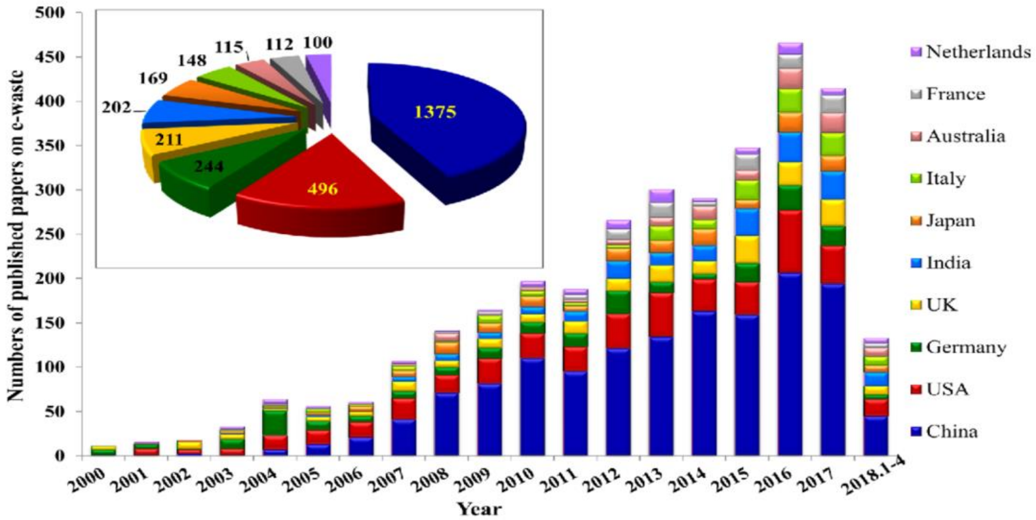

Figure 1.2 — Trend and contribution of peer-reviewed papers on e-waste topic published by top 10 countries from 2000 until 2018 [4]

1.5. Paper electronics as an alternative

The advantages of paper-based substrates are their high availability, cheap cost, portability, lightweight, biodegradability, and environmental friendliness. Because of these benefits, paper has become an unavoidable substrate for a wide range of electronic devices such as solar cells, radio frequency identification (RFID) tags, microfluidic glucose sensors, flexible displays, micro-electromechanical systems (MEMS), touch sensors, foldable passive components and circuits, and energy storage devices. [5] [6] [7]

Paper substrates are among the most promising alternatives for flexible, affordable, and environmentally friendly electronic devices, because future mass production will require fast and mature procedures to develop genuine commercial products. [8]

Also, cellulosic paper is the world's lightest and cheapest substrate material, as well as the planet's most important biopolymer and a major source of worldwide economic activity. [9]

Furthermore, paper is a recyclable material, leading to the reduction in the use of scarce resources, and the finished devices may be readily disposed of by simple incineration. Despite all of the unmatched advantages listed, paper electronics now have inescapable downsides. The characteristics of paper, for example, are greatly dependent on humidity and temperature, necessitating precise condition control. [8]

1.6. Mechanical Energy Harvester

Mechanical energy harvester or mechanical nanogenerator is the energy harvesting process, where the energy harvester accumulates mechanical energy from the ambient environment in any forms (such as vibration, motion, human movements, air flow etc.) and convert it into electrical energy.

These energy harvester are being touted as potential independent power sources for low-power electronic devices such as wireless sensors, portable electronics, and medical implants through integrated with energy harvesting and transducing systems, where energy is harvested from ambient sources [10] This self-powered technology thereby alleviate difficulties associated with batteries, such as limited lifespan, huge size, pollution, and high maintenance costs. [11]

From last decades, triboelectric or piezoelectric materials are already being explored in this area by different research groups. In this particular, conjugated polymer like polyaniline, polypyrrole is a unique choice because they have a unique combination of hard (metal like) and soft (organic like) matter, which can be exerted to convert mechanical stimuli to electrical energy. [11]

1.7. Polypyrrole (PPy) and Charger Transfer Mechanism

Polypyrrole (PPy), the conjugated polymer that is explored during this master thesis work for functionalized recycled paper substrate to design energy harvester. The interesting feature of conjugated polymers like PPy is that the chemical and physical properties this polymer can easily be modified through doping-dedoping processes. Because of that conjugated polymers are used in different kind of smart applications such as electronics, energy storage, energy harvester, sensors, etc… [11] [12]

Moreover, the pyrrole monomer has a good environmental stability and great redox properties that make it easy to oxidize, is soluble in some common solvents (including water), that makes the materials very stable in the ambient atmosphere.

PPy is attractive because of its properties such as: high conductivity; strong redox activity; easy processability; great thermal and electrochemical stability; low toxicity for the environment. [13] The use of such polymers in the energy harvesting devices relies on the fact that PPy has a structural disorder and electrical properties that exhibit both metallic and semiconductor behavior. [14]

PPy has been frequently synthesized through chemical/electrochemical polymerization. However, pure PPy is brittle and somewhat difficult to process. [15] [16]

In this this master thesis work, PPy has been explored as an efficient energy harvester by showing its charge transfer mechanism. PPy has the role of being a charge transfer mediator.

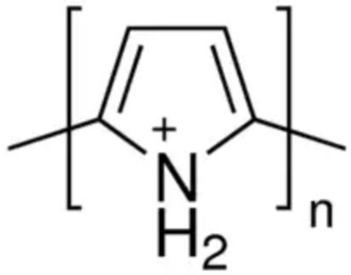

Figure 1.3 - Chemical structure of Polypyrrole [17]

Charge transfer mechanism is a mechanism that enables the generation of electrical energy from mechanical energy.

When pressure is applied to the device, the polymer chains bend, causing an increase in the local electrical density, which causes "Fermi level pinning". [18] This causes the charges to transition from the active layer to the charge collection layer.

When the pressure is released, the polymer reverts to its original structure, resulting in a charge shortage in the area where the pressure was applied. The "hoping mechanism" compensates for the lack of charges by transferring charges from surrounding polymer chains to the region where the electron density is scarce (**Figure 1.4**).

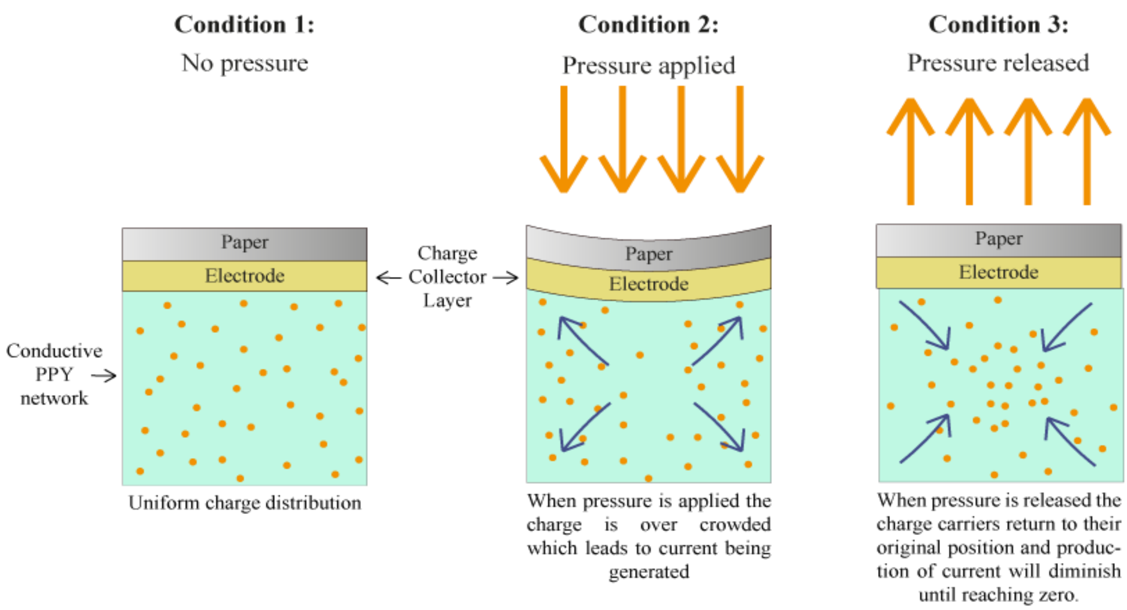

Figure 1.4 - Synthesis of the process of charge transfer mechanism in 3 conditions: No Pressure; Pressure applied; Pressure released

2.
Materials and Methods

2.1. Obtaining cellulose from waste paper

The source for the cellulose fibers was old newspapers. To obtain the fibers, small pieces of paper were blended with water and mixed thoroughly. After blending, the paste obtained was filtered (ø 200 mm) to strain out the water as possible to obtain cellulose. The wet cellulose paste was then heated in the oven and left for at least 12h (More information in **Annex A.1.1**).

2.2. Production of cellulose-matrices for electronic application

2.2.1. Cellulose substrates made in water / ethanol systems

The recycle paper produced are produced in the medium of water/ethanol systems (with a different weight ration). The amount of Cellulose used was 0.83g (0.5% Cellulose) which was the best weight (**Annex A.1.2.4**.). To make the substrates, water and ethanol were mixed in a blender and then put in the sonicator for 45min to mix everything. After, the solution with the cellulose fibers dispersed was filtrated and the recycled paper substrates dried overnight in the oven to completely dry. The following weight percentages of Ethanol to Water were used: 0%; 20%; 50%; 80%; 100%. This corresponds to: 0 g; 32 g; 80 g; 128 g; 160 g (**Table 2.1**).

Table 2.1 — Ethanol/Water percentage and corresponding weight

Ethanol	160 g (100%)	132 g (80%)	80 g (50%)	32 g (20%)	0 g (0%)
Water	0 g (0%)	32 g (20%)	80 g (50%)	132 g (80%)	160 g (100%)

2.2.2. Paper functionalization with PPy

Before the functionalization with PPy the recycled paper substrates were cut into small squares of $2cm\ x\ 2cm$. This was done to ease the process and make the process of functionalization quicker.

For the functionalization the following solutions were used:

- **Solution A:** 10 ml Distilled Water; 1.3g APS (Ammonium persulfate); 125µl HCl
- **Solution B:** 20 ml Distilled Water; 200µl Pyrrole.

These two solutions were mixed with ice around to reduce the reaction time which were then applied to the paper substrates whether it's in Drop-cast or Dipping.

In terms of the functionalization, a 1:2 Volume Ratio was used: 1 for Solution A and 2 for Solution B. Which translates to 12µl of solution A and 24µl of solution B (More information in **Annex A.1.7**).

After functionalization, the paper with PPy was left to dry for about 24h.

2.3. Production of electrodes

To design the electrodes for the energy harvester device, the screen-printing technique was used. Whatman paper has been used for printing the electrode layer. Silver (CRSN2442 AG INK, Coated Screen Inks) and carbon (CRSN2664 C INK, Sun Chemical) ink was deposited on the Whatman paper by screen printing technology. The inks were cured on a hot plate 30-60 minutes. More information in **Annex A.1.8**)

2.4. Fabrication of the device

For the fabrication of the energy harvester device the electrode is combined and joins together with the paper that was functionalized. Everything is then wrapped in Whatman paper using a small adhesive tape. Whatman paper was put both on top and below (**Figure 3.17**). The top and bottom layer will have Whatman Paper. In the middle are the functionalized recycled paper substrate with PPy (which is an active layer) and another layer with electrode (which is silver or carbon printed paper substrate) next to it.

2.5. Characterization Techniques

The scanning electron microscope (**SEM TM3030**) was used for examining and analyzing the morphology of microstructure. [19] Energy dispersive spectroscopy (**EDS**) used with SEM to determine the chemical elements present in the recycled paper substrate.

Fourier transform infrared (**FTIR**) spectroscopy was used for the measurement of the absorption (or transmission) of infrared radiation as a function of wavelength number. This was used for investigating the functional group present in a given recycled paper substrate.[20] Measurements of weight, thickness and area were also made to determine density and porosity.

For electrical analysis an **oscilloscope** was used to measure the voltage and current (IV-Curves) (Open Circuit Voltage and Short Circuit Current) and o**rigin** program to obtain the graphs and values. (More information in **Annexes A.2** and **A.3**).

3. Results and Discussion

3.1. Chemical and Morphology Analysis of cellulose substrates

Cellulose is a biomaterial that is found in nature and is extensively employed in the biomedical industry. It's abundant, easy to regenerate, and biodegradable. [21]

Despite being hydrophilic, cellulose is insoluble in water and difficult to dissolve with conventional organic solvents due to intermolecular and intramolecular hydrogen bonding between the hydroxyl groups of nearby cellulose strands. [21]

Since of its low solubility, cellulose is an excellent biomaterial for tissue engineering because it can withstand physiological conditions. [21]

In regards to ethanol, its qualities allow it to be used as a dehydrating agent during treatment before drying. It has been demonstrated that it improves the quality of dried products and speeds up the drying process. [22]

Given that water and ethanol have been demonstrated to connect with cellulose, it would be interesting to explore what would happen if varying percentages of these two components were combined in paper made from old newspapers and broken down to their purest form.

3.1.1. Morphology and properties of cellulose-substrates: ethanol and water dependency

In this section, recycled paper substrates that contain ethanol and water (with varying percentages) were made and thoroughly examined.

But before examining the paper substrates manufactured out of recycled cellulose fibers, a small drop of ethanol contacting recycled cellulose fibers was dropped in silicon to see if the fibers and substrates are comparable (**Figure 3.1**). This was made to serve as a reference point for understating the size and shapes of the fibers.

From observing one of the SEM images the average length of the fibers tends to be 1 mm with and Standard deviation of 0.32mm. This was done by taking 10 measurements of these recycled paper substrates.

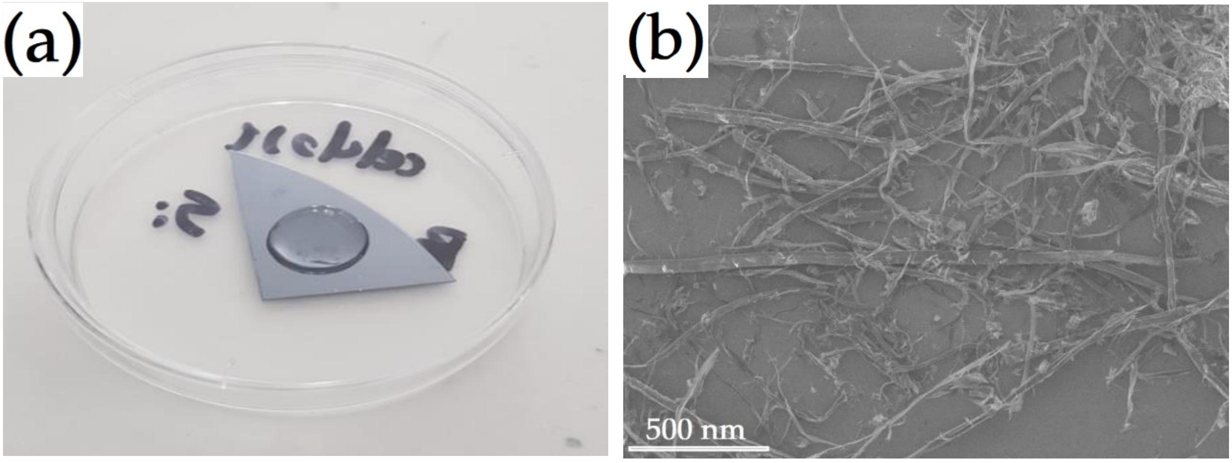

Figure 3.1 — Recycled paper substrate with a small drop of Ethanol with cellulose fibers on silicon – (a) Recycled paper substrate on Silicon (b) Cellulose fibers present in the recycled paper substrate obtained from SEM imaging

The recycled cellulose fibers from newspaper as mentioned before, has been used as a raw materials resource for manufacturing new paper substrates, with different percentages of water and ethanol as a solvent medium.

As mentioned previously (**Materials and Methods 2.2.)**, these recycled paper substrates (recycled paper substrate) are the final result of the process using only the white part of the newspaper. Compared with the other portions of the newspaper which contains inks (as a pictures or texts form), the white part shows good functionality with PPy. It can be assumed that the colored part of the newspaper contains several organic dyes as an ink.

In our low-cost recycling approaches, the de-inked mechanism was not used.

It is possible to see in **Figure 3.2** the recycled paper substrates (without any type of functionalization and also no reagents) that with an increase in ethanol lead to an increase in the roughness of the recycled paper substrate (as clearly noticed from the photographic images of each recycled paper substrate shown in Figure 3.2).

In the recycled paper substrate with no ethanol, there is no major surface roughness when considering the recycled paper substrates with 80% and 100% of ethanol. There are many lumps can be observed throughout the paper surface for higher ethanol percentage.

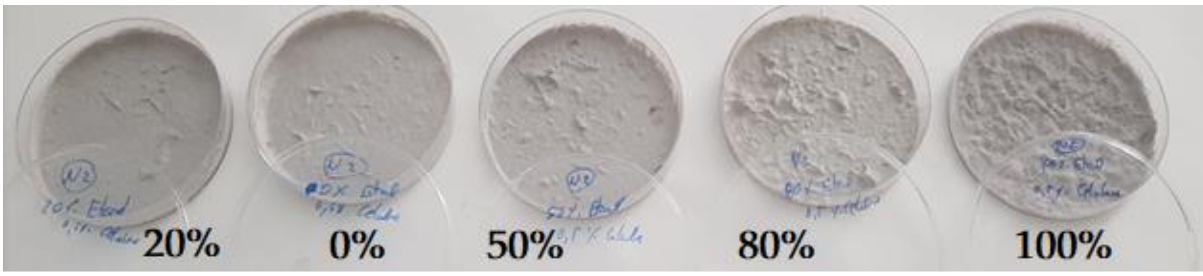

Figure 3.2 — Pictures of 5 Recycled paper substrates. From left to right: 20% Ethanol; 0% Ethanol; 50% Ethanol; 80% Ethanol; 100% Ethanol

Also, in the blending process, it was noted that recycled paper substrates prepared with higher contents of ethanol and less water required a bit more time in the blender. While for recycled paper substrates with water the blender was turned on for about 30 seconds.

The recycled paper substrates with a higher percentage of Ethanol required up to 2 minutes of blending in order to obtain a better dispersion of the fibers in the solvent system of blending.

Figure 3.3 is the resulting SEM imaging (surface and cross-section) of the recycled paper substrate with just Water and no Ethanol.

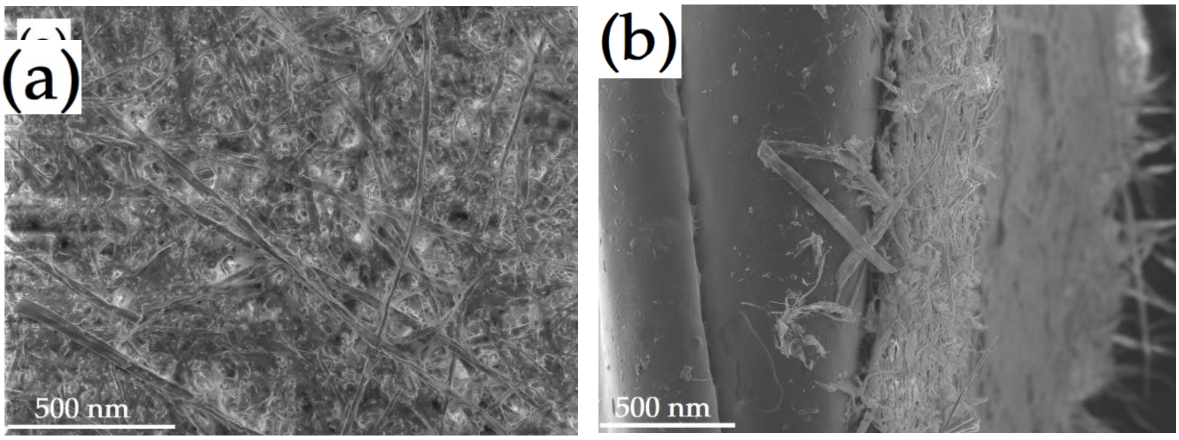

Figure 3.3 — SEM image - 0.5% Cellulose – 100% Water and 0% Ethanol - (a) Substrate surface (b) Cross-section

The variation of the amount of solvents leads not only to different morphologies of the substrate but also change properties such as density and porosity of the recycled paper substrates.

In order to measure these characteristics, the recycled paper substrates were cut into squares of $2cm\ x\ 2cm$. Then, the recycled paper substrates were weighed on a scale and the thickness was measured with a micrometer.

The formulas that were used for these calculations are the:

- Formula for volume: $V = Height * 2 * 2\ \ cm^3$;
- Formula for density: $\rho = \frac{m}{v}\ (\frac{g}{cm^3})$ where m is mass an v is volume
- Formula to obtain porosity $P = \left(1 - \frac{\rho(b)}{\rho(a)}\right) * 100\ \%$, where $\rho(b)$ is the density of the recycled paper substrate in question and $\rho(a)$ is the density of cellulose. [23]

This was done considering the density of cellulose (In Bulk) was: 1.5 $gcm^{-3.}$ [24] . The resulting values of density are of raw material Density.

The resulting tables from these calculations are **Table 3.1.1** and **Table 3.1.2.**

Table 3.1.1 — Density and porosity of the Ethanol and Water recycled paper substrates from white part of newspaper

Samples	Thickness (mm)	Mass (g)	Volume (cm^3)	Density ($\frac{g}{cm^3}$)	Porosity (%)
0% Ethanol	0.29	0.06	0.12	0.52	65
20% Ethanol	0.48	0.03	0.18	0.19	87
50% Ethanol	0.89	0.04	0.36	0.11	83
80% Ethanol	0.54	0.05	0.22	0.22	85
100% Ethanol	0.55	0.04	0.22	0.17	88

In **Table 3.1.1,** the volume and density is the highest with the recycled paper substrate with no Ethanol whatsoever. Also, that with just a small increase in Ethanol from the recycled paper substrate with just water to the one with 20% Ethanol, the porosity increase by a huge number (From 65.398% to 87.334%).

The same findings can be found with the colored newspaper parts which are presented in **Table 3.1.2**. This was done to find if a similar pattern happened (in relation to the white part of the newspaper).

The density was highest with the recycled paper substrate with no Ethanol and porosity was the lowest. From the recycled paper substrates with 0% Ethanol to 20% Ethanol there was a big jump of 16.81% (From 74.92% to 91.73).

This also confirms that the same pattern occurred. As said before, when there is an increase in Ethanol and decrease Water (in terms of percentage) recycled paper substrates that have more lumps and increase in porosity are obtained. This may be due to different ways Ethanol and Water connect to Cellulose.

Table 3.1.2 — Density and porosity of the Ethanol and Water recycled paper substrates taken from colored newspaper

Samples	Thickness (mm)	Mass (g)	Volume (cm^3)	Density ($\frac{g}{cm^3}$)	Porosity (%)
0% Ethanol	0.31	0.04	0.12	0.38	75
20% Ethanol	0.55	0.03	0.22	0.12	92
50% Ethanol	0.55	0.04	0.22	0.20	87
80% Ethanol	0.58	0.04	0.23	0.16	90
100% Ethanol	0.61	0.06	0.24	0.26	83

Also, the color changes because when the recycled paper substrates that contain ethanol and water are filtered the color stays in the recycled paper substrates, as seen in **Figure 3.4**.

With an increase in ethanol there is also an increase in the color that remains in the recycled paper substrates. This was only relevant to the recycled paper substrates that were cut from the colored parts of the original newspaper.

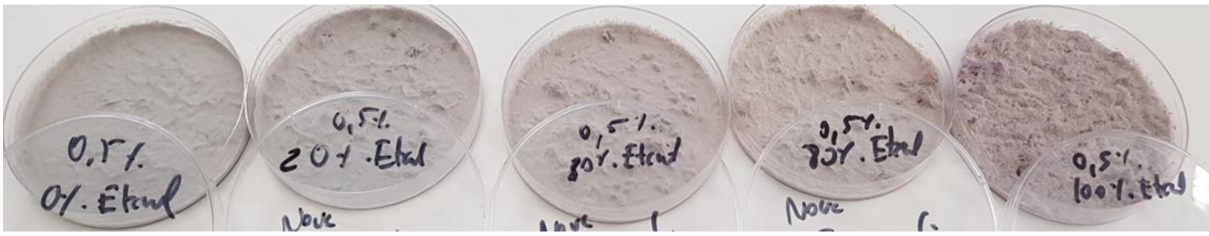

Figure 3.4 — Picture of recycled paper substrates obtained from colored newspaper. From left to right: 0% Ethanol; 20% Ethanol; 50% Ethanol; 80% Ethanol; 100% Ethanol. This was obtained from colored newspaper unlike the others which came from just the black and white parts

3.2. Functionalization of substrates with PPy

The recycled paper substrates were then functionalized with PPy. The functionalization procedure is straightforward and quick and results in the interaction of multiple reduced and oxidized monomer blocks. It was chosen to use the Oxidative Chemical polymerization (COP) for this functionalization. [25] APS was the oxidizing agent used.

The two methods used were the Drop-cast method and the Dipping method (Both in Situ) (More information in **Annex A.1.7**). Both were used to be later tested and to see what influence they would have on results from Morphological and Electrical Analysis.

The polymerization of PPy happened for 24h which was the time for the recycled paper substrates to completely dry. Also, there was no washing step included in this process. [26]

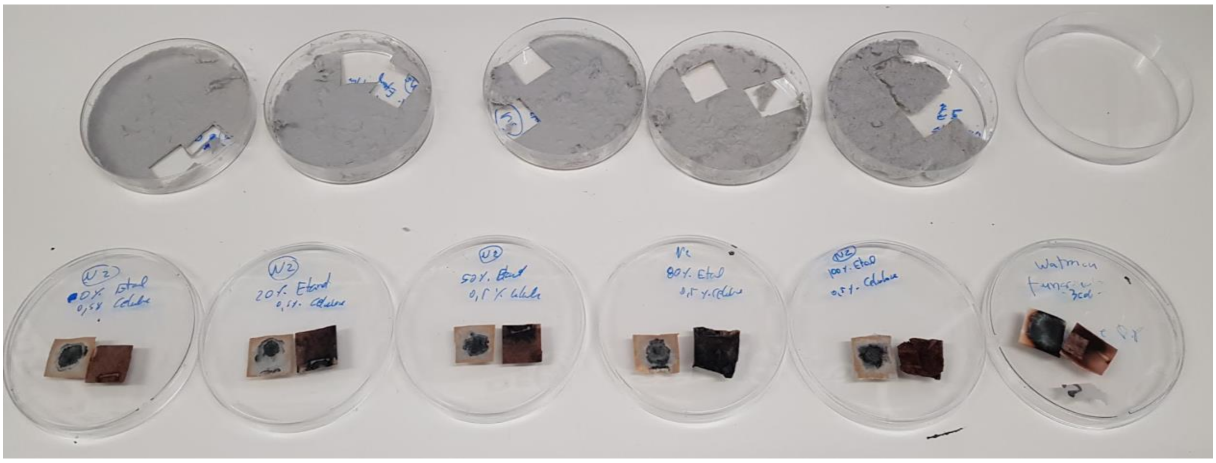

Figure 3.5 — Picture of multiple recycled paper substrates with varying degrees of Ethanol being left to dry after functionalization with PPy. The small recycled paper substrates on the left are the one that were put through Drop-cast and the right one was the one that went through the Dipping process. From the left to right: 0% Ethanol; 20% Ethanol; 50% Ethanol; 80% Ethanol; 100% Ethanol; Whatman paper.

Figure 3.5, are presented the samples with varying levels of ethanol and water.

With the comparison, it can be noticed from the Figure 3.5, that the entire samples were functionalized while using dipping approaches. With the drop-cast technique, solvent penetrates all over the paper substrates throughout the cellulose network. Due to the use of 100% recycled cellulose fibers to fabricate new recycled paper substrate, the fibers length and arrangement are not in well ordered (can be observed in SEM morphological images). Therefore with drop-cast approach, there may have been fibers that were not fully functionalized in the center of the samples with PPy. But the wettability was more prominent in samples with Dipping.

The following images (**Figure 3.6** to **Figure 3.10**) are of SEM of the first recycled paper substrates with varying percentages of ethanol and water. These were done to analyze what happened to the fibers after they were functionalized with PPy. This is useful for comparing them to the images of the fibers after they were made and properly functionalized.

The left images of the figures (**Figure 3.6** to **Figure 3.10**) are those that went through the dipping process, while the right images of the same figures are the fibers that were drop-cast. All images are of the surface of the substrate.

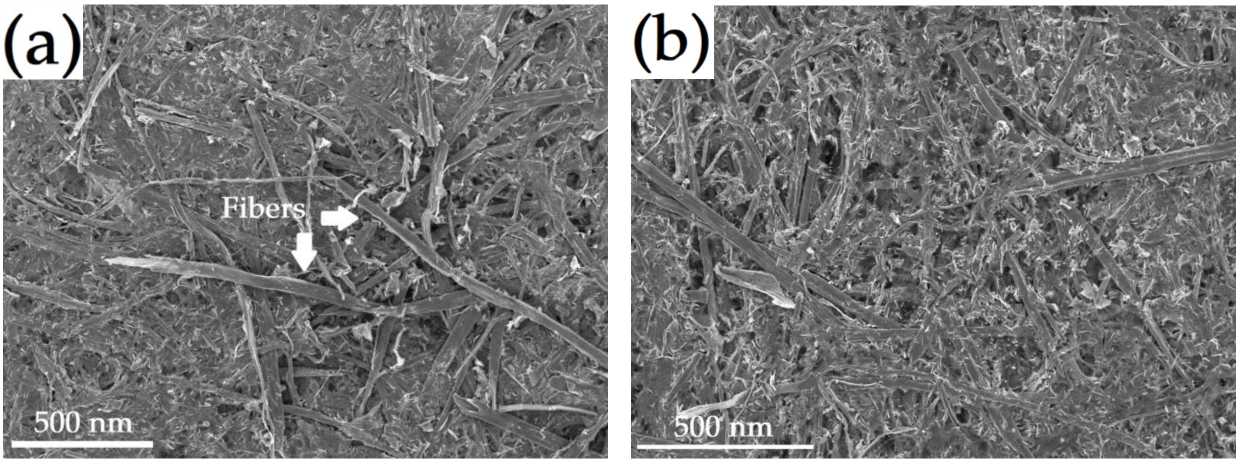

Figure 3.6 — SEM - Surface of recycled paper substrate with 0% Ethanol with PPy.
(a) Dipping method (b) Drop-cast method

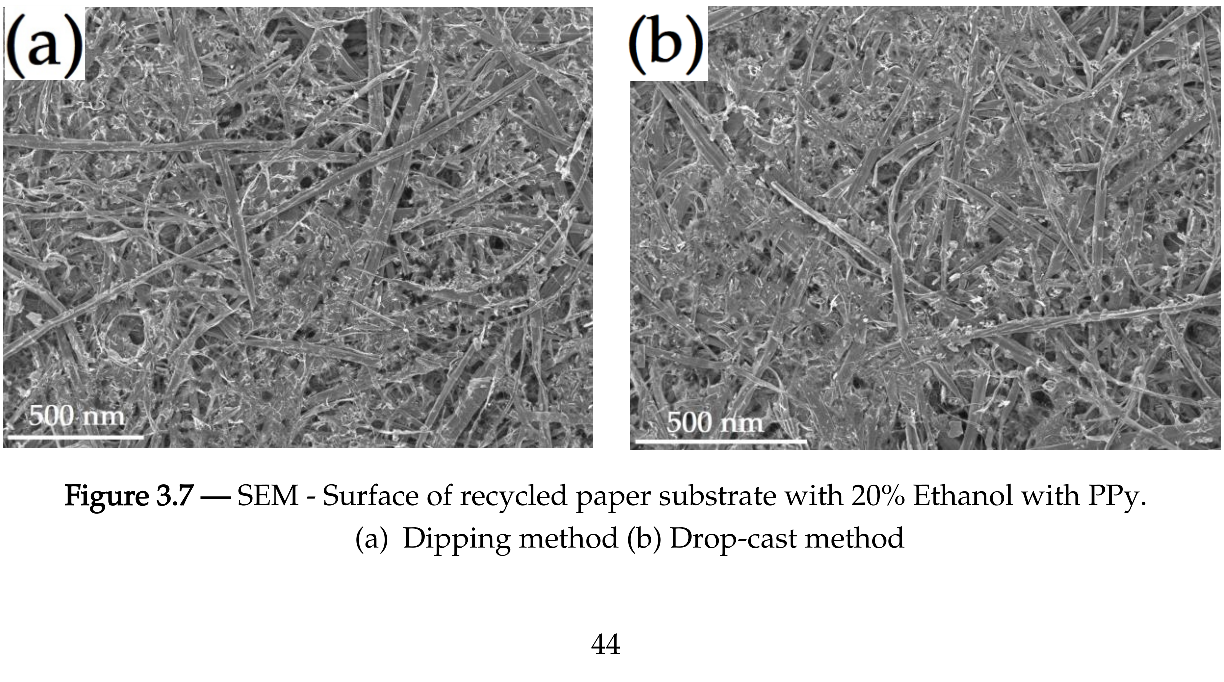

Figure 3.7 — SEM - Surface of recycled paper substrate with 20% Ethanol with PPy.
(a) Dipping method (b) Drop-cast method

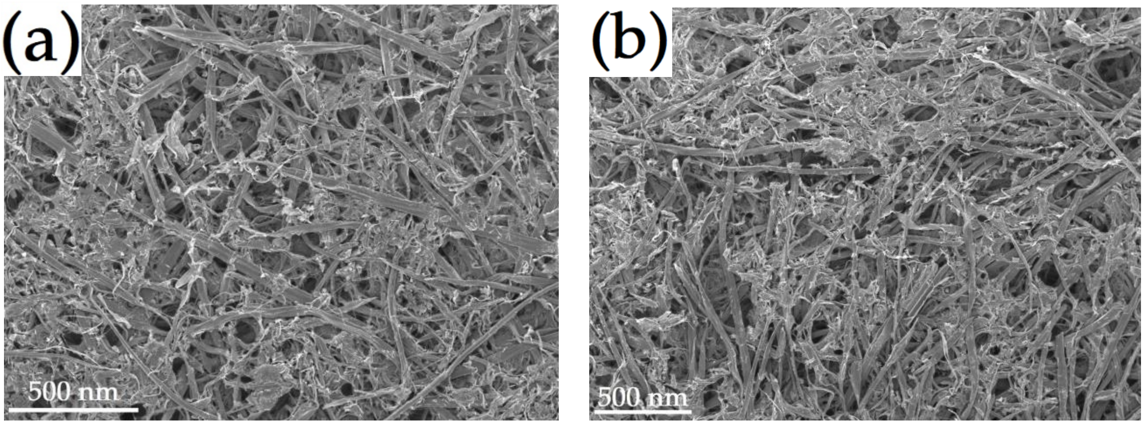

Figure 3.8 — SEM - Surface of recycled paper substrate with 50% Ethanol with PPy.
(a) Dipping method (b) Drop-cast method

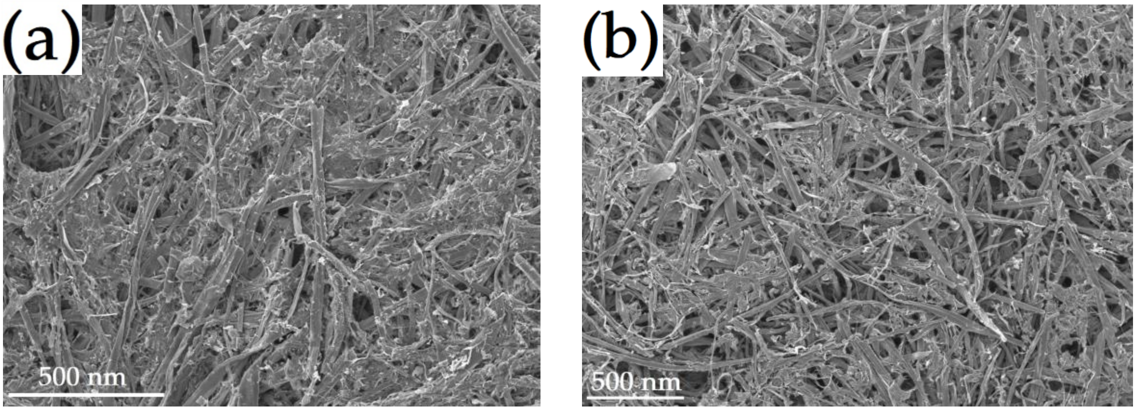

Figure 3.9— SEM - Surface of recycled paper substrate with 80% Ethanol with PPy.
(a) Dipping method (b) Drop-cast method

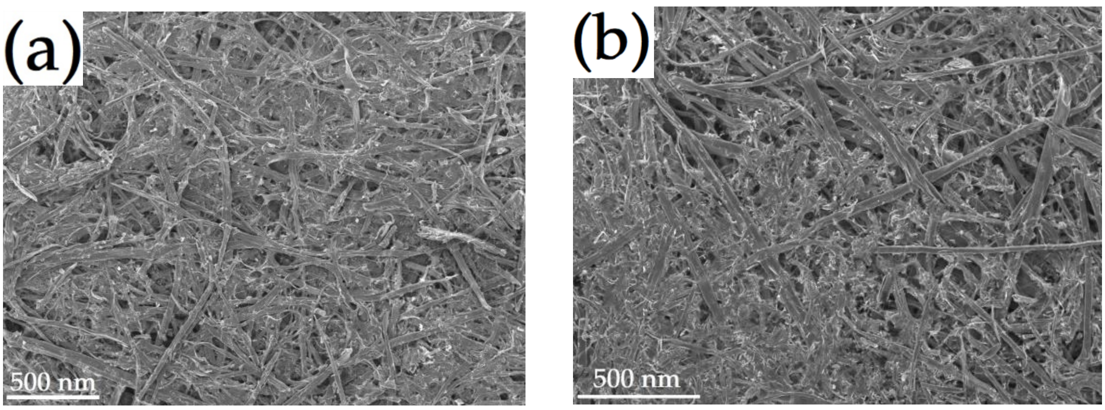

Figure 3.10 — SEM - Surface of recycled paper substrate with 100% Ethanol with PPy.
(a) Dipping method (b) Drop-cast method

It is observable (**Figure 3.6** to **Figure 3.10**) that the pictures have similarities between them even though they are composed of different values of ethanol and water in their composition.

Also, comparing the dipping and drop-cast methods, there is no substantial difference in terms of the fibers and their overall structure. (More pictures in **Annex A.2.2** to **Annex A.2.4**)

In **Figure 3.11** is a SEM picture of Whatman paper (containing no Water or Ethanol) that was decided to functionalize with PPy. This was done to serve as reference point as the Whatman paper did not go through the blending process and other processes that the substrates went through.

It is possible to see that the fibers appear to have less loose ends and there are no major "holes" in the structure compared to the recycled paper substrates from **Figure 3.6** to **Figure 3.10.** This is due to Whatman paper not going through the blending process.

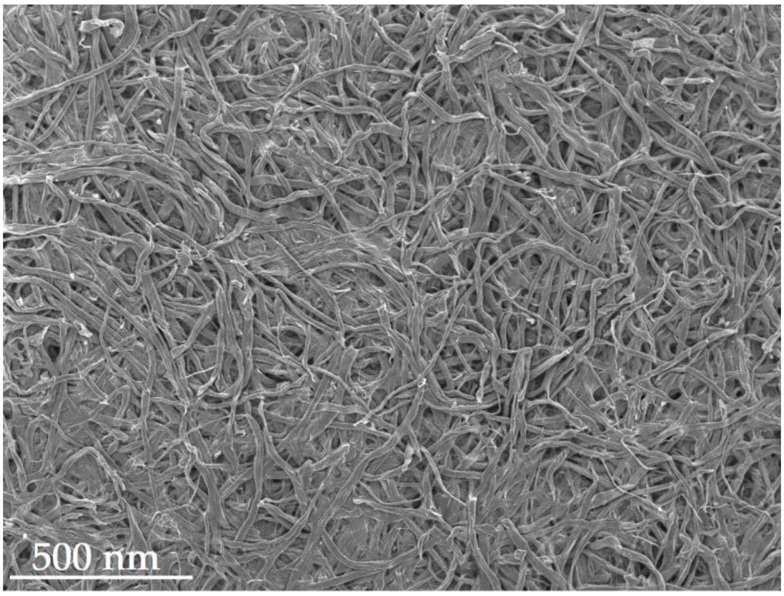

Figure 3.11 — SEM Picture - Whatman paper functionalized with PPy

The analytical technique of energy-dispersive x-ray spectroscopy was used for the elemental analysis of a recycled paper substrate. It is based on the analysis of the interaction between an x-ray source and a recycled paper substrate. Each characterization skills are largely attributable to the fundamental premise that each element has a unique atomic structure, resulting in unique sets of peaks on its x-ray spectrum. [27]

In **Figure 3.12**, it is shown an area of the substrate surface that was used for the SEM-EDS analysis. The elements are also displayed with color to be able to differentiate from one another.

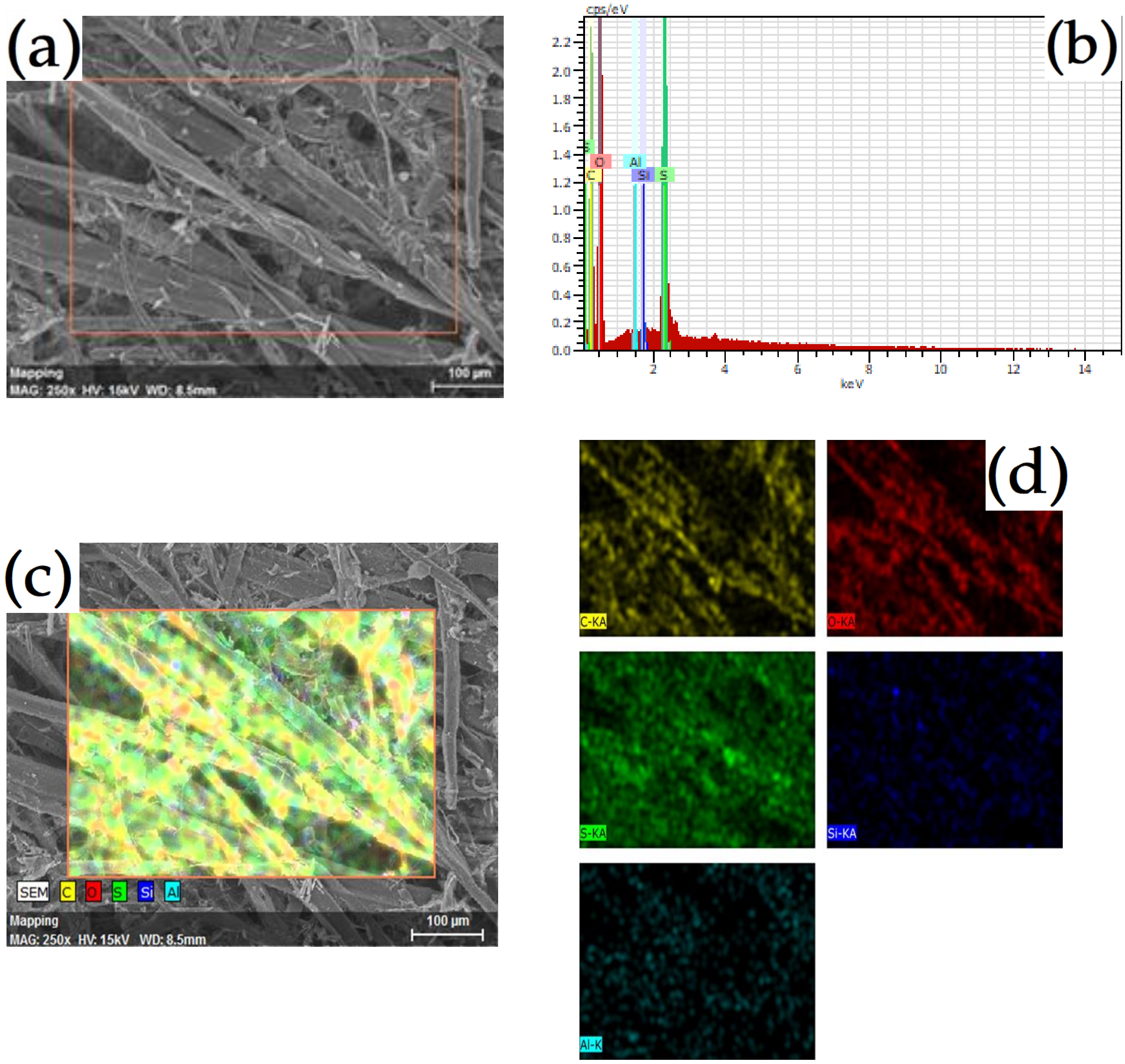

Figure 3.12 — SEM-EDS Analysis of recycled paper substrate with 0% Ethanol (Only water). (a) SEM picture of area chosen for SEM-EDS analysis (b) Graph of elements found in the area for analysis (c) SEM picture of area chosen for SEM-EDS analysis with elements in being represented in color (d) Color of the elements - Yellow/Carbon; Red/Oxygen; Sulfur/Green. Dark Blue/ Silicon; Light Blue/Aluminum

From **Figure 3.12,** it is possible to see that the elements that sand out are carbon, oxygen, sulfur, silicon and aluminum.

The values of the **Table 3.2** were taken from SEM-EDS analysis and put on the table for better comprehension as it is necessary to determine precisely what the percentages of the elements are present in the corresponding recycled paper substrates.

Table 3.2 - Element percentages of the Ethanol recycled paper substrates and Whatman Paper (%)

Recycled paper substrate / Element (%)	Carbon	Oxygen	Sulfur	Silicon	Aluminum	Calcium
0% Ethanol Dipping	39.24	51.45	8.89	0.24	0.18	N/A
0% Ethanol Drop-cast	N/A	N/A	N/A	N/A	N/A	N/A
20% Ethanol Dipping	38.44	52.43	8.01	0.47	0.19	0.46
20% Ethanol Drop-cast	50.62	48.15	0.97	0.25	0.01	N/A
50% Ethanol Dipping	33.62	58.97	12.04	0.25	0.19	0.07
50% Ethanol Drop-cast	48.74	48.55	0.93	0.93	0.30	0.55
80% Ethanol Dipping	N/A	N/A	N/A	N/A	N/A	N/A
80% Ethanol Drop-cast	46.49	48.59	2.77	0.31	0.09	1.65
100% Ethanol Dipping	37.70	60.49	12.11	0.19	0.03	N/A
100% Ethanol Drop-cast	46.41	48.45	2.7	0.22	0.16	1.59
Whatman Dipping	43.77	55	1.22	N/A	N/A	N/A
Whatman Drop-cast	39.21	58.13	2.65	N/A	N/A	N/A

From the table **(Table 3.2)**, the main Elements that stand out from the others are carbon and oxygen which comes mainly from cellulose and PPy itself. The presence of sulfur is only due to use of APS during the polymerization. Some few amounts of aluminum and calcium may be coming from the recycled cellulose fibers which were used from the newspapers. Though, because of using recycled lab-scale paper substrate (where the fibers lengths and distribution is not completely homogenous) the percentage of elemental mapping cannot be totally quantified. Unfortunately, there were 2 recycled paper substrates (0% Ethanol Drop-cast and 80% Ethanol Dipping) that were not possible to analyze and consequently obtain values. Therefore they are presented in the table as N/A (Non applicable).

The mathematical procedure (Fourier transform) is used in Fourier transform infrared spectroscopy (FTIR) to transfer the raw into the actual spectrum. The infrared spectrum of transmission or absorption of a recycled paper substrate and the presence of organic and inorganic chemicals are obtained using the FTIR method. [20] Two FTIR analyses were done.

The first was done with recycled paper substrates not functionalized with PPy which are seen in **Figure 3.13.** The second analysis was after the functionalization with PPy (Both Dipping and Drop-cast method of 100% Ethanol) which corresponds to **Figure 3.14.** All analysis is of the absorbance of the recycled paper substrates. These were made using the program **origin**.

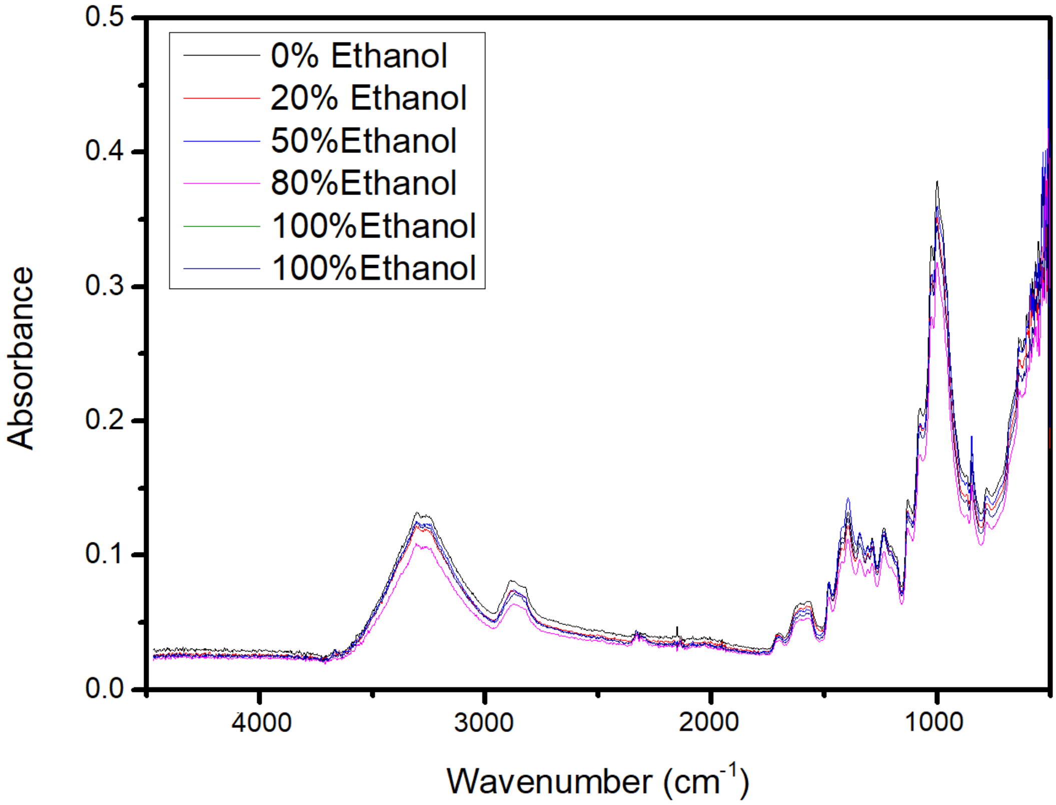

Figure 3.13 - FTIR analysis of all recycled paper substrates and paper from the newspaper used (Not functionalized) – Origin

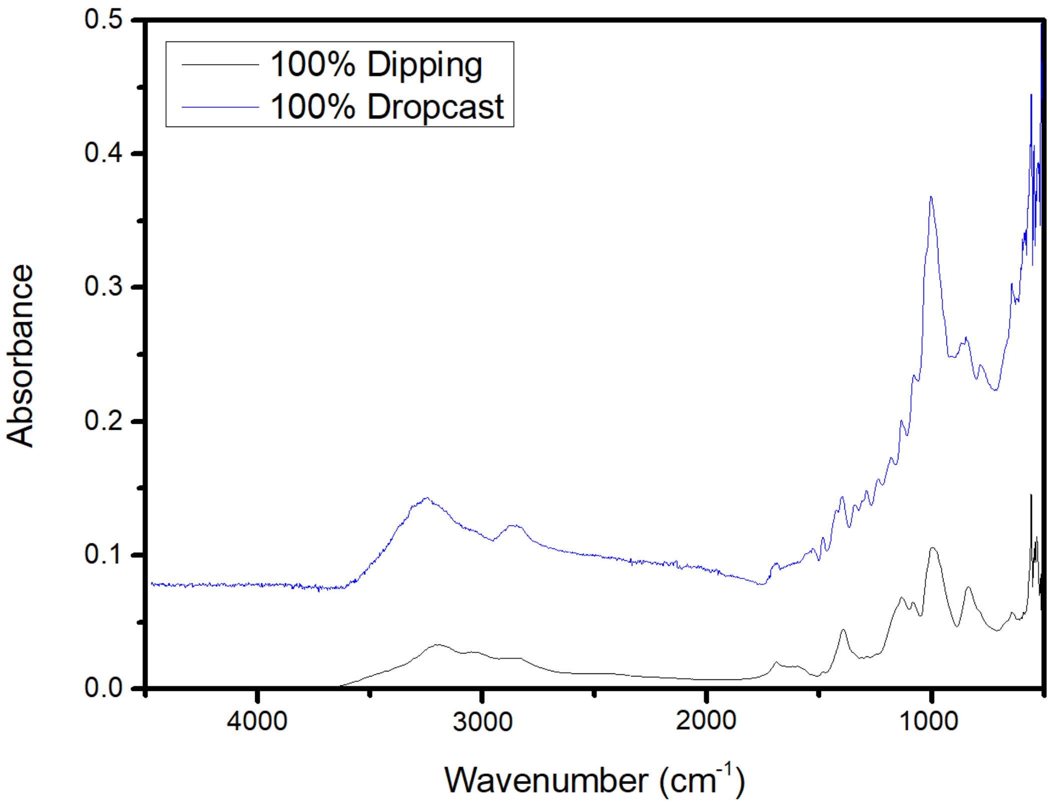

Figure 3.14 - FTIR analysis of 100% Dipping and 100% Drop-cast paper substrates (Functionalized with PPy) - Origin

In **Figure 3.13** and **Figure 3.14** there is a common pattern appear where there is a peak around wavenumbers: 3300 cm-1; 1000 cm-1; 200 cm-1.

In **Figure 3.14** the absorbance is higher for dipping than it is for drop-cast. And the peaks are also higher.

For all the recycled paper substrates, it is possible to conclude that there are main peaks that contain C=O stretching (acid halide) and O-H stretching (alcohols). [28] This due to the majority of paper being made up of organic components, such as carbon, hydrogen, and oxygen (C, H and O).

C–H wiggling is responsible for the peaks around 1000 cm-1. C=C stretching is represented by peaks around 1500 cm-1, whereas C=N and C–N bonds are represented by peaks at around 1600 cm–1 and 1300 cm–1.

The presence of N–H stretching vibrations is attributed to the development of tiny peaks at 3300 cm–1. The peaks detected in this study are consistent with those found in similar literature. [29] [30] [31]

There may also be some presence of Amine (N-H) and Carbon Dioxide (O=C=O) which corresponds, respectively, to 3500 cm–1 and 2349 cm–1,

Other graphs related to FTIR (including individual recycled paper substrates) were also made and can be found in **Annex A.2.5**.

3.3. Electrical Analysis

The purpose of the electrical analysis of the recycled paper substrates was to determine the best values and to which recycled paper substrates they corresponded to.

In **Figure 3.15** is the technical drawing of the recycled paper substrate and the actual recycled paper substrates that were tested.

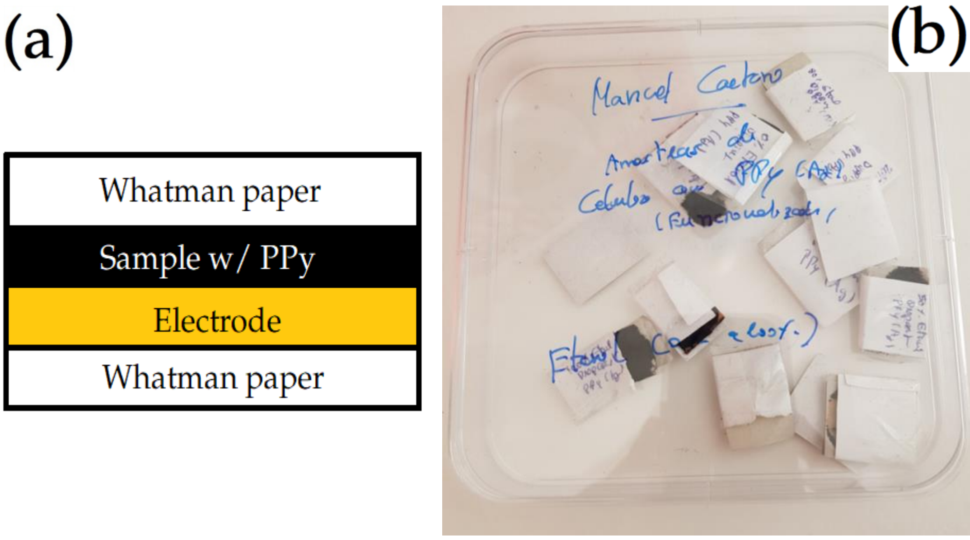

Figure 3.15 — (a) Drawing of the device (b) Box where all recycled paper substrates that formed the device where kept to then be used for Electrical Characterization.

To check the conductivity of the samples an oscilloscope was used and two types of circuits: Open-Circuit and Closed-circuit. In **Figure 3.16** is a drawing of the whole setup with full-wave rectifier circuits.

Also, to obtain the electricity the samples were tapped with an index finger (using moderate force). In both instances, 5 pictures were taken from the oscilloscope (Short Circuit Current and Open Circuit Voltage).

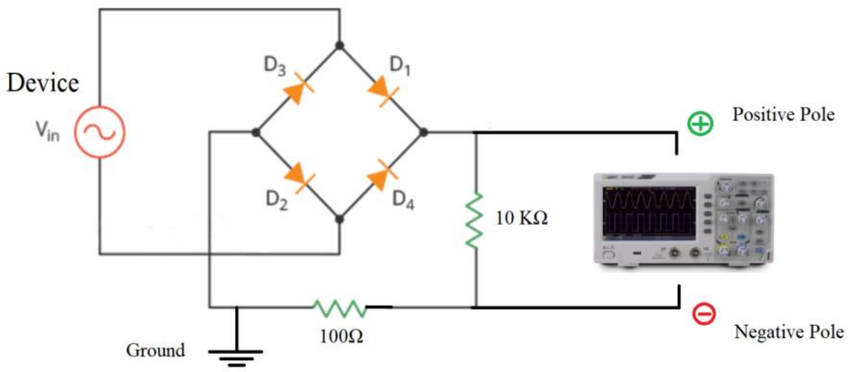

Figure 3.16 — Drawing of the whole setup used for Electrical Characterization

The voltage was measured in the oscilloscope when an index finger was exerting pressure against the system (**Figure 3.17**). The recycled paper substrate was glued to the floor to make sure it was stable.

The force was mild and although it is impossible to be very precise and consistent as sometimes more or less force was used. The force used and the tapping pattern were as consistent (and as rhythmic) as possible to obtain the most accurate information for analysis.

To obtain the current a resistance was needed so that it was possible to use Ohm Law($V = RI$). This Resistance had the value of: $R = 10\ M\Omega$.

The analysis of values and consequently the creation of graphs (**Figure 3.18** and **Figure 3.19**) were all done using the computer program **origin**.

Only the top 3 peaks of each of the five photos were considered for measuring the values. And, after obtaining these values, the average of these peaks was done.

As said before, this was done all the five photos (five photos for each recycled paper substrate) obtained from the Oscilloscope. When using an Open Circuit Voltage it is expected to get higher and lower peaks than in the Short Circuit Current setup.

Both (Short Circuit Current and Open Circuit Voltage) measurements helped determine which of the recycled paper substrates (with the varying percentages of Ethanol) were the best. (Another example can be found in **Annex A.3**).

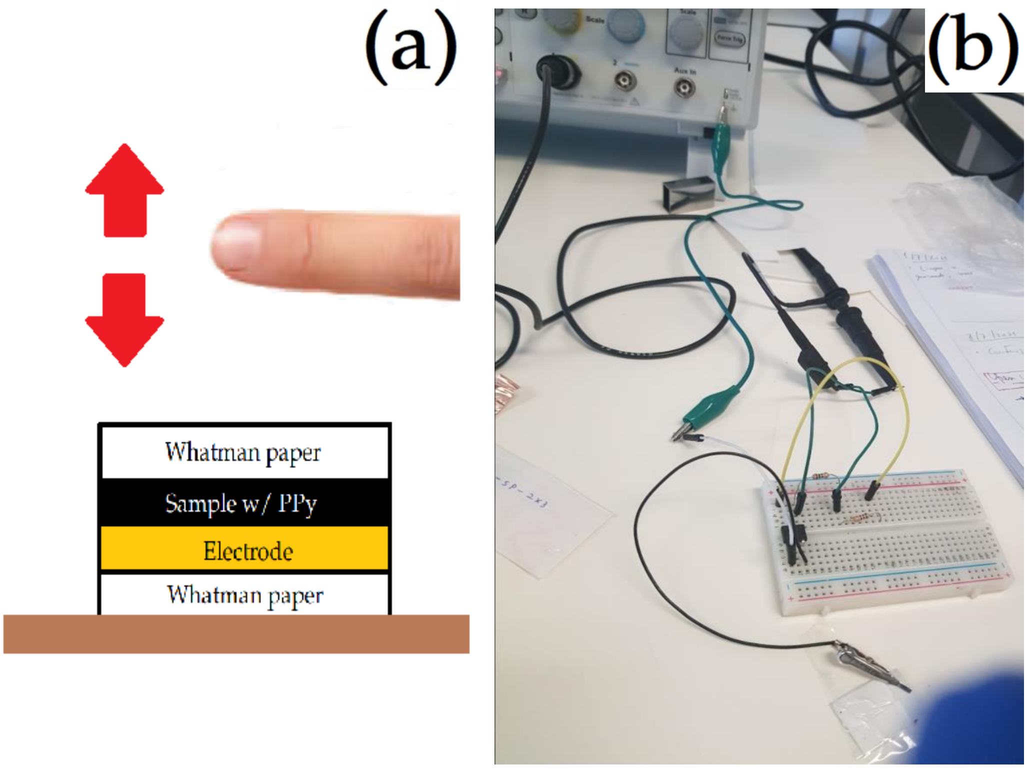

Figure 3.17 — (a) Index finger moving up and down to put pressure in the recycled paper substrate that is laid on the table (b) Photo taken of the setup of the whole circuit for Electrical Analysis

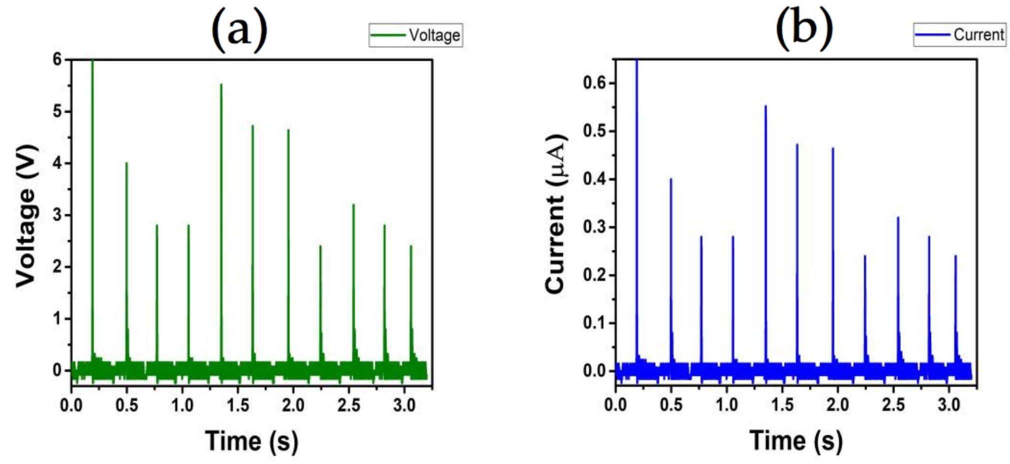

Figure 3.18 — Example of graph obtained from 0% Ethanol with the Dipping method – Short Circuit Current - (a) Graph of Voltage and Time (b) Graph of Current and Time. Obtained from Graph (a)

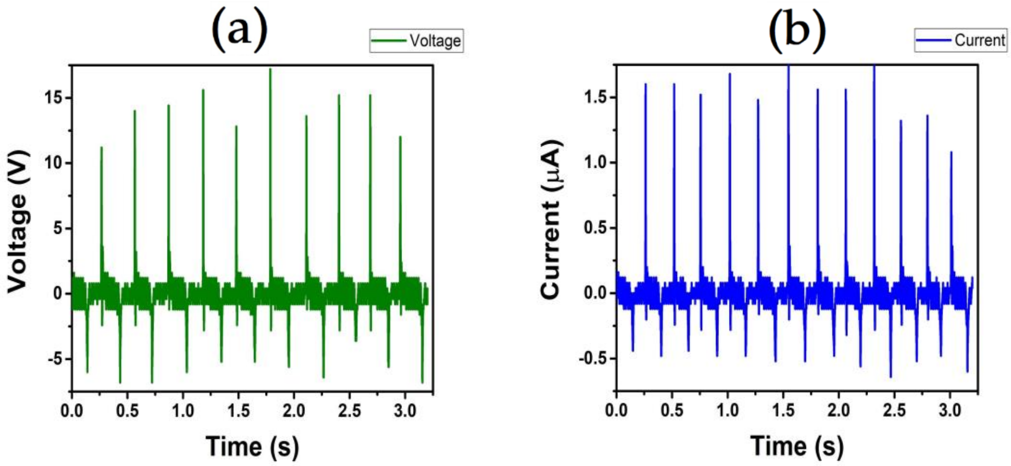

Figure 3.19 — Example of graph obtained from 0% Ethanol with the Drop-Cast method – Open Circuit Voltage - (a) Graph of Voltage and Time (b) Graph of Current and Time. Obtained from Graph (a)

Considering all of the charts and taking all the averages, It was decided to put them on a table so that it can be accurately compared the values and determine which of the recycled paper substrates presented the highest values. The variation in peaks of **Figure 3.18** and **Figure 3.19** are due to finger pressure which can never be completely precise due to human error.

The values of were analyzed to try and find a clear and distinct "winner" in terms of the highest value and see if it is possible to determine if Dipping is better or worse than Drop-cast as a method for the functionalization of the substrates with PPy.

The negative values are due to the charge traveling attempting to achieve electrostatic stability. Because the movement of this charge carrier is in the opposite direction due to scarcity, it generates a voltage or current with the opposite polarity. [32]

The following tables (**Table 3.3.1** and **Table 3.3.2)** are of the values obtained with Silver as an electrode. And (as said before) all these recycled paper substrates were functionalized with PPy.

Table 3.3.1 - Average Currents (I) (µA) – Dipping

	Short Circuit Current (µA)	Open circuit Voltage (µA)
0% Ethanol	0.77	1.80
20% Ethanol	0.50	1.11
50% Ethanol	0.63	0.28
80% Ethanol	0.35	1.05
100% Ethanol	0.24	1.23

In **Table 3.3.1** are the values for the Dipping process in terms of their average currents. In **Table 3.3.2** are the values for the Drop-cast process in terms of their average currents.

Table 3.3.2 - Average Currents (I) (µA) – Drop-cast

	Short Circuit Current (µA)	Open circuit Voltage (µA)
0% Ethanol	0.22	1.07
20% Ethanol	0.46	0.97
50% Ethanol	0.29	0.79
80% Ethanol	0.23	0.90
100% Ethanol	0.16	1.34

From both tables (**Table 3.3.1** and **Table 3.3.2**) it is clear that the Dipping method produces far better results. This may be due to the recycled paper substrate being fully would lead to more conduction of electricity as there is more PPy present that in Drop-cast.

In a Short Circuit Current, all the recycled paper substrates in Dipping achieved higher values. In the Open Circuit Voltage, the recycled paper substrates 50% and 80%, and 100% produced better results in Drop-cast, but the other two were better in Dipping.

It is also possible to see that the recycled paper substrates with 0% Ethanol were the best out of all the others by a large margin, especially if we consider only using the Dipping process. Achieving values of $I = 0.7675\ \mu A$ in Short Circuit Current and $I = 1.8027\ \mu A$ in Open Circuit Voltage.

Considering that it is in our best interest to seek the highest value of current it appears that the recycled paper substrate with 0% Ethanol and 100% water was better. And it is also better that if it was decided to functionalize again this substrate (considering these values for water and ethanol) it is better to use the Dipping process compared to the Drop-cast method.

4.
Conclusion and Future prospects

In this paper, it was shown how to obtain a successful Energy Harvesting device that is flexible, low-cost, and that was made from entirely recycled paper which came from old newspapers and was later functionalized successfully with polypyrrole (PPy).

Some interesting conclusions were also reached, such as the fact that in the filtration process (and when using colored parts from the newspaper), Ethanol did not remove the color from the colored newspaper while water did.

It was also demonstrated that polypyrrole (PPy) was a good polymer to be functionalized to use for building this device and putting ice around the solutions while performing the functionalization, was a good idea as it slowed down the reaction and allowed for a slower and more efficient functionalization.

The best method to functionalize this paper was shown to be the Dipping method, which gave better results than the Drop-cast method but also made the structure of the recycled paper substrate a bit weaker. This means that even though the Dipping process was better, it is not without its disadvantages. Also, the element Sulfur was much more present in the Dipping method due to the higher presence of APS.

Silver was shown to be a good conductor of electricity to use for this device and that was put on whatman paper (with Screen Printing) gave us solid values in the electrical analysis.

Ethanol was proven to be worse than water for the device but it did show it strengthening the fibers so perhaps an ideal percentage would be around 90% water and 10% Ethanol. This would be a good area to explore as perhaps smaller percentages of Ethanol such as 5% or even 2% would produce even better recycled paper substrates.

Future prospects also include are trying to upscale the whole process and produce recycled paper substrates that are bigger and larger. All this process was made using recycled paper substrates that were a few *cm* long. It would be interesting to try and scale up the recycled paper substrates.

Also, another idea for the future could be using other reagents such as Nitric Acid or Ammonia and other type of equipment for building this device. There is a lot of scientific literacy of various combinations of reagents and techniques used related to cellulose and paper, so there could be an interesting way to make different recycled paper substrates that could potentially produce better devices.

References

[1] X. Wang, C. Yao, F. Wang, and Z. Li, "Cellulose-Based Nanomaterials for Energy Applications," *Small*, vol. 13, no. 42, pp. 1–19, 2017, doi: 10.1002/smll.201702240.

[2] PACE, "A New Circular Vision for Electronics: Time for a Global Reboot," *World Econ. Forum*, no. January, pp. 1–24, 2019, [Online]. Available: www.weforum.org.

[3] WHO, *Children and digital dumpsites*. 2021.

[4] J. Fu, H. Zhang, A. Zhang, and G. Jiang, "E-waste Recycling in China: A Challenging Field," *Environ. Sci. Technol.*, vol. 52, no. 12, pp. 6727–6728, 2018, doi: 10.1021/acs.est.8b02329.

[5] M. H. Zulfiqar, K. Riaz, and T. Tauqeer, "Foldable, Eco-Friendly and Easy Go Designed Paper Based Supercapacitor: Energy storage Device," *Proc. 2020 17th Int. Bhurban Conf. Appl. Sci. Technol. IBCAST 2020*, no. January, pp. 40–43, 2020, doi: 10.1109/IBCAST47879.2020.9044591.

[6] S. M. Khan, J. M. Nassar, and M. M. Hussain, "Paper as a Substrate and an Active Material in Paper Electronics," *ACS Appl. Electron. Mater.*, vol. 3, no. 1, pp. 30–52, 2021, doi: 10.1021/acsaelm.0c00484.

[7] W. Zhang *et al.*, "Integrating van der Waals materials on paper substrates for electrical and optical applications," *Appl. Mater. Today*, vol. 23, p. 101012, 2021, doi: https://doi.org/10.1016/j.apmt.2021.101012.

[8] Y. Lin, D. Gritsenko, Q. Liu, X. Lu, and J. Xu, "Recent Advancements in Functionalized Paper-Based Electronics," *ACS Appl. Mater. \& Interfaces*, vol. 8, no. 32, pp. 20501–20515, 2016, doi: 10.1021/acsami.6b04854.

[9] R. Martins, I. Ferreira, and E. Fortunato, "Electronics with and on paper," *Phys. status solidi – Rapid Res. Lett.*, vol. 5, no. 9, pp. 332–335, 2011, doi: https://doi.org/10.1002/pssr.201105247.

[10] T. L. Stott and M. O. Wolf, "Electronic interactions in metallated polythiophenes: what can be learned from model complexes," *Coord. Chem. Rev.*, vol. 246, no. 1–2, pp. 89–101, Nov. 2003, doi: 10.1016/S0010-8545(03)00114-0.

[11] J. Janata and M. Josowicz, "Conducting polymers in electronic chemical sensors," *Nat. Mater.*, vol. 2, pp. 19–24, 2003, doi: 10.1038/nmat768.

[12] P. P. and S. Karpagam, "Conjugated polymers – a versatile platform for various photophysical, electrochemical and biomedical applications: a comprehensive review," 2021.

[13] D. Ateh, H. Navsaria, and P. Vadgama, "Polypyrrole-Based Conducting Polymers and Interactions with Biological Tissues," *J. R. Soc. Interface*, vol. 3, pp. 741–752, 2007, doi: 10.1098/rsif.2006.0141.

[14] E. Buhks and I. M. Hodge, "Charge transfer in polypyrrole," *J. Chem. Phys.*, vol. 83, no. 11, pp. 5976–5980, 1985, doi: 10.1063/1.449630.

[15] A. Kausar, "Chapter 5 - Perspectives on nanocomposite with polypyrrole and nanoparticles," in *Conducting Polymer-Based Nanocomposites*, A. Kausar, Ed. Elsevier, 2021, pp. 103–128.

[16] A. G. MacDiarmid, “Polyaniline and polypyrrole: Where are we headed?,” *Synth. Met.*, vol. 84, no. 1, pp. 27–34, 1997, doi: https://doi.org/10.1016/S0379-6779(97)80658-3.
[17] “Polypyrrole,” [Online]. Available: https://www.sigmaaldrich.com/PT/en/product/aldrich/481114?gclid=Cj0KCQjw4uaUBhC8ARIsANUuDjVkOy1B7QRiNt3F0GiJWekydOF7BRgKkTShk9STyH_90LgblJv504YaAsRCEALw_wcB.
[18] C. Tengstedt, W. Osikowicz, W. Salaneck, I. Parker, C.-H. Hsu, and M. Fahlman, “Fermi-level pinning at conjugated polymer interfaces,” *Appl. Phys. Lett.*, vol. 88, p. 53502, 2006, doi: 10.1063/1.2168515.
[19] W. Zhou, R. Apkarian, Z. L. Wang, and D. Joy, “Fundamentals of scanning electron microscopy (SEM),” *Scanning Microsc. Nanotechnol. Tech. Appl.*, pp. 1–40, 2007, doi: 10.1007/978-0-387-39620-0_1.
[20] P. Mohamed Shameer and P. Mohamed Nishath, “Chapter 8 - Exploration and enhancement on fuel stability of biodiesel: A step forward in the track of global commercialization,” in *Advanced Biofuels*, A. K. Azad and M. Rasul, Eds. Woodhead Publishing, 2019, pp. 181–213.
[21] O. S. Manoukian *et al.*, “Biomaterials for Tissue Engineering and Regenerative Medicine,” in *Encyclopedia of Biomedical Engineering*, R. Narayan, Ed. Oxford: Elsevier, 2019, pp. 462–482.
[22] J. Zubernik, M. Dadan, J. Cichowska, and D. Witrowa-Rajchert, “The Impact of the Pre-Treatment in Ethanol Solution on the Drying Kinetics and Selected Properties of Convective Dried Apples,” *Int. J. Food Eng.*, pp. 1–11, 2019, doi: 10.1515/ijfe-2018-0338.
[23] L. Y. Mwaikambo and M. P. Ansell, “The determination of porosity and cellulose content of plant fibers by density methods,” *J. Mater. Sci. Lett.*, vol. 20, no. 23, pp. 2095–2096, 2001, doi: 10.1023/A:1013703809964.
[24] National Center for Biotechnology Information, “No Title,” 2022, [Online]. Available: https://pubchem.ncbi.nlm.nih.gov/compound/Cellulose.
[25] A. Yussuf, M. Al-Saleh, S. Al-Enezi, and G. Abraham, “Synthesis and Characterization of Conductive Polypyrrole: The Influence of the Oxidants and Monomer on the Electrical, Thermal, and Morphological Properties,” *Int. J. Polym. Sci.*, vol. 2018, 2018, doi: 10.1155/2018/4191747.
[26] G. Ferreira, S. Goswami, S. Nandy, L. Pereira, R. Martins, and E. Fortunato, “Touch-Interactive Flexible Sustainable Energy Harvester and Self-Powered Smart Card,” *Adv. Funct. Mater.*, vol. 30, no. 5, pp. 1–9, 2020, doi: 10.1002/adfm.201908994.
[27] M. Abd Mutalib, M. A. Rahman, M. H. D. Othman, A. F. Ismail, and J. Jaafar, “Chapter 9 - Scanning Electron Microscopy (SEM) and Energy-Dispersive X-Ray (EDX) Spectroscopy,” in *Membrane Characterization*, N. Hilal, A. F. Ismail, T. Matsuura, and D. Oatley-Radcliffe, Eds. Elsevier, 2017, pp. 161–179.
[28] “IR Spectrum Table & Chart.” https://www.sigmaaldrich.com/PT/en/technical-documents/technical-article/analytical-chemistry/photometry-and-reflectometry/ir-spectrum-table.
[29] C. Saravanan, R. C. Shekhar, and S. Palaniappan, “Synthesis of polypyrrole using benzoyl peroxide as a novel oxidizing agent,” *Macromol. Chem. Phys.*, vol. 207, no. 3, pp. 342–348, 2006, doi: 10.1002/macp.200500376.
[30] M. A. Chougule, S. G. Pawar, P. R. Godse, R. N. Mulik, S. Sen, and V. B. Patil, “Synthesis and Characterization of Polypyrrole (PPy) Thin Films,” *Soft Nanosci. Lett.*, vol. 01, no. 01, pp. 6–10, 2011, doi: 10.4236/snl.2011.11002.
[31] S. Ahmad, I. Khan, A. Husain, A. Khan, and A. M. Asiri, “Electrical conductivity based ammonia sensing properties of polypyrrole/mos2 nanocomposite,” *Polymers (Basel).*, vol. 12, no. 12, pp. 1–14, 2020, doi: 10.3390/polym12123047.

[32] S. Goswami *et al.*, "Human-motion interactive energy harvester based on polyaniline functionalized textile fibers following metal/polymer mechano-responsive charge transfer mechanism," *Nano Energy*, vol. 60, no. April, pp. 794–801, 2019, doi: 10.1016/j.nanoen.2019.04.012.
[33] P. Sirviö, J. Sidaravicius, R. Maldzius, K. Backfolk, and E. Montrimas, "Effect of NaCl and Moisture Content on Electrical and Dielectric Properties of Paper," *J. Imaging Sci. Technol. - J IMAGING SCI TECHNOL*, vol. 53, 2009, doi: 10.2352/J.ImagingSci.Technol.2009.53.2.020501.
[34] M. Hietala, K. Varrio, L. Berglund, J. Soini, and K. Oksman, "Potential of municipal solid waste paper as raw material for production of cellulose nanofibres," *Waste Manag.*, vol. 80, pp. 319–326, 2018, doi: https://doi.org/10.1016/j.wasman.2018.09.033.
[35] N. Ghaemi, S. S. Madaeni, A. Alizadeh, P. Daraei, V. Vatanpour, and M. Falsafi, "Fabrication of cellulose acetate/sodium dodecyl sulfate nanofiltration membrane: Characterization and performance in rejection of pesticides," *Desalination*, vol. 290, pp. 99–106, 2012, doi: https://doi.org/10.1016/j.desal.2012.01.013.
[36] P. Widsten, N. Dooley, R. Parr, J. Capricho, and I. Suckling, "Citric acid crosslinking of paper products for improved high-humidity performance," *Carbohydr. Polym.*, vol. 101, no. 1, pp. 998–1004, Jan. 2014, doi: 10.1016/j.carbpol.2013.10.002.
[37] F. J. Higgins and G. E. Ho, "Hydrolysis of cellulose using HCl: A comparison between liquid phase and gaseous phase processes," *Agric. Wastes*, vol. 4, no. 2, pp. 97–116, 1982, doi: https://doi.org/10.1016/0141-4607(82)90019-1.

A. Annex

A.1. Materials and Methods

A.1.1. Blending process

Saúde

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A nossa boca pode esconder doenças gastrointestinais não diagnosticadas?

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Existem várias doenças que se manifestam por sinais e sintomas na cavidade oral. As doenças que envolvem o sistema digestivo podem começar a ser detetadas por alterações na boca. Muitas vezes, é na ida ao médico dentista que se descobrem, o que possibilita um diagnóstico e uma ida a um gastroenterologista mais precoces.

As doenças gastrointestinais mais comuns e diagnosticáveis na boca incluem a doença intestinal inflamatória - doença de Crohn e colite ulcerativa -, a doença celíaca, a doença do refluxo gastroesofágico, as neoplasias do trato gastrointestinal, entre outras.

A doença intestinal inflamatória tem como sintomas intestinais a dor abdominal, diarreia, hemorragia retal e ainda perda de peso e má nutrição. As lesões orais podem preceder, coincidir ou suceder ao início dos sintomas intestinais. Essas manifestações são pouco frequentes, mas podem ser a única evidência de doença, sendo mais comuns na doença de Crohn do que na colite ulcerativa. As manifestações orais podem incluir: aftas/úlceras persistentes, edema (inchaço) labial/gengival, mau hálito, diminuição da saliva, dificuldade em engolir, candidíase (infeção fúngica), etc. Há uma maior prevalência para aumento de cáries e da doença periodontal.

A doença celíaca pode originar diarreia crónica, dor abdominal, vómitos, perda de peso, anemia, perda de apetite, fadiga, irritabilidade, etc. Como manifestações orais, as mais comuns são os defeitos na estrutura dos dentes, nomeadamente na camada de esmalte, diminuição da salivação, alteração da normal aparência da língua, rouquidão, etc. Quanto à prevalência de cárie, há menor propensão para o desenvolvimento de cárie, devido à restrição dietética.

A doença do refluxo gastroesofágico, geralmente, manifesta-se através de refluxo, azia, dor gástrica, etc. Na cavidade oral, o sinal mais comum é a erosão dos dentes, devido ao contacto direto com o ácido gástrico, sabor amargo inexplicável, mau hálito, perda de sabor, alteração do fluxo de saliva, "céu da boca" mais avermelhado e irritado, etc. É importante o diagnóstico precoce desta doença, uma vez que é um fator de risco para o cancro oral. Quando a erosão dentária se torna mais severa, pode ser observado um grande aumento da sensibilidade dentária ao frio, assim como uma diminuição da estética dos dentes. Normalmente, os desgastes dentários por problemas gastrointestinais ocorrem nos dentes posteriores (molares e pré-molares). Não se devem confundir estes desgastes dentários com os que ocorrem por trauma de escovagem ou por consumo de alimentos/bebidas muito ácidos.

Relativamente às neoplasias/tumores do trato gastrointestinal, estes podem metastizar para a região oral. Pacientes com metástases (principalmente mandibulares) podem ser assintomáticos ou podem queixar-se de dor, inchaço, parestesia, dificuldade em engolir ou mobilidade dentária.

Assim, os médicos dentistas podem ser o primeiro profissional de saúde a diagnosticar doenças gastrointestinais, através de uma correta observação à cavidade oral, principalmente em casos em que a doença não se manifesta de outras formas.

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Figure A.1.1 – Picture of a newspaper and different sections used for obtaining paper. (1) Piece of paper cut with black ink (2) Piece of paper cut for white paper (3) Piece of paper with color

Figure A.1.1 is an example of a newspaper used for obtaining cellulose. The newspaper is dived in 3 sections in order to obtain three different types of paper. The part of the paper that was most important was the one cut from section 2. This was also the zone that was most valuable to us.

Figure A.1.2 is a collection of images taken during the whole process of obtaining cellulose.

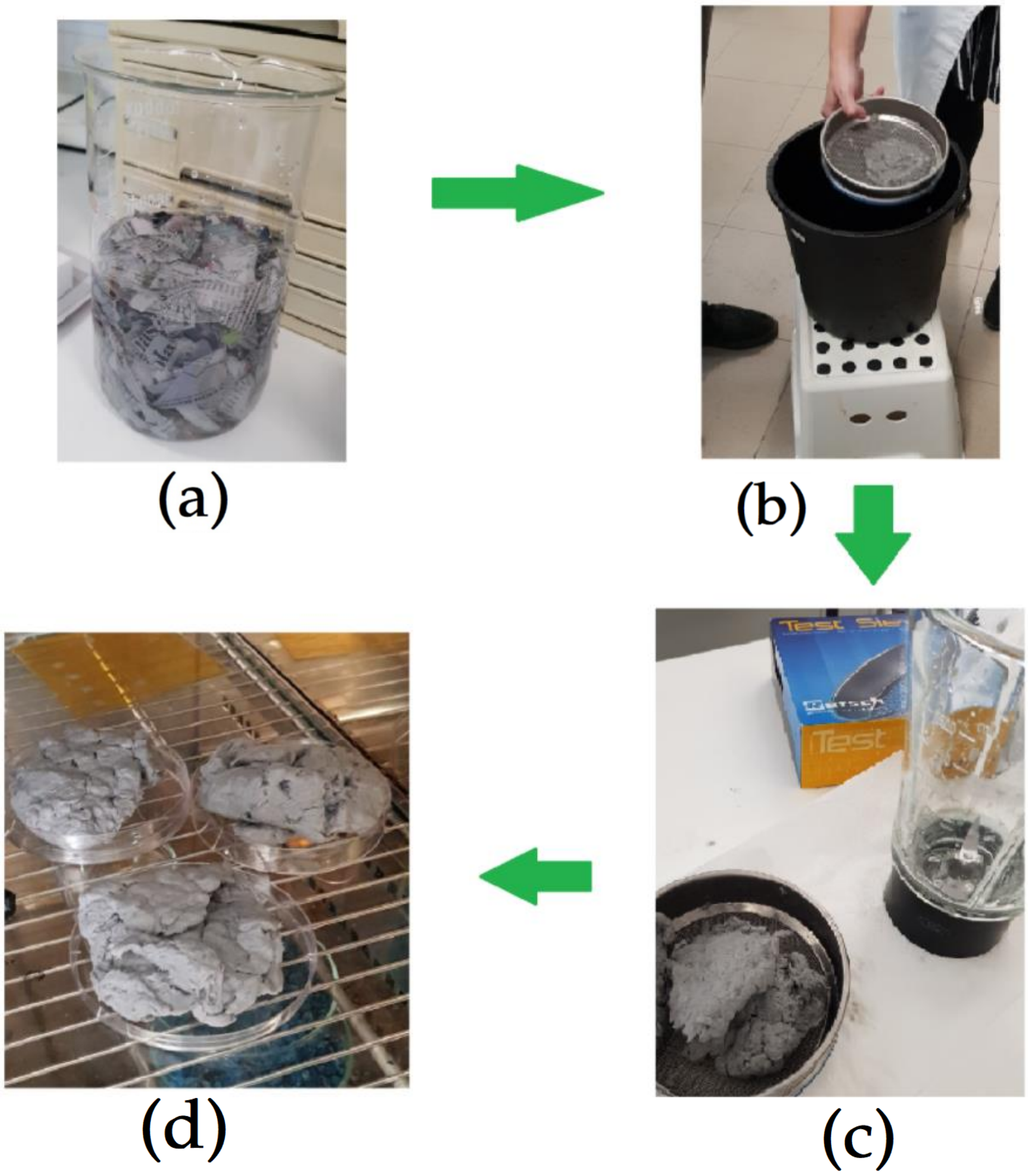


Figure A.1.2 – Process to obtain cellulose in 4 pictures: a) Paper with water. b) Filtration process c) Blender and the filter used in this process d) Cellulose being put in the oven

A.1.2. Substrates containing the reagents: NaCl; SDS; CA

This section is related to some experiments done with NaCl; SDS; CA that were performed in the beginning of this Dissertation.

These were simply experiments to test the effects of regents in the substrates. This was done before focusing on ethanol and water as the main components of the dissertation.

A.1.2.1. Production of cellulose mix with ionized water

Before using reagents different percentages of molecular weight were chosen to then to experiment and decide which one was best.

The following percentages were used: 1%: 2%; 3%; 0.1%; 0.2%; 0.5%. These percentages are related to the 160mL of water that was added (**Table A.1**).

Table A.1 — Molecular weight of cellulose and corresponding weight in grams

Weight of cellulose	1.66g (1%)	3.32g (2%)	4.98g (3%)	0.166g (0.1%)	0.322g (0.2%)	0.83g (0.5%)

A.1.2.2. Reagents used (NaCl; SDS; CA)

After obtaining cellulose, the following reagents were used to make new paper: SDS - Sodium dodecyl sulfate; CA - Citric acid; NaCl - Sodium chloride.

Different percentages of these reagents were used to obtain the best recycled paper substrate possible. For the recycled paper substrates with ethanol and water, reagents were not used.

Salts like NaCl (in addition to the moisture content of the paper), are employed in papermaking to control the qualities of electrophotographic papers and guarantee that they meet the requirements for the correct level of static electricity and toner transfer.

NaCl was used firstly because the addition of NaCl causes a significant drop in the surface and volume resistivity of paper. The addition of NaCl also raises the moisture content of the paper. [33] There was also a previous paper where Sodium was used for the processing of waste paper, so NaCl has already been used with paper. [34]

When a little amount of SDS is added to the casting solution, the top-layer and sublayer membranes become significantly thinner and more porous than CA membranes. Adding SDS thickens the layer of cellulose. Also, SDS has an amphiphilic structure (i.e., it has a hydrophilic head and a hydrophobic tail). As a result, a layer of SDS molecules forms on the casting film's surface, slowing the formation of the highly concentrated polymer on the casting film by reducing the rate of solvent outflow SDS also reduces the interaction between polymer chains by forming a polymer-surfactant complex. As a result, the skin layer's growth is slowed, and macro voids form in the suppository. [35]

Also, compressive strength can increase with a dose of CA. The CA molecule can be attached to cellulose by one ester bond (no crosslink) or two ester bonds (intra- or interfiber crosslink). Increased inter and intrafiber crosslinking, as well as reduced moisture uptake, can significantly increase the compressive strength after CA treatment. Also, CA treatment without an extra curing catalyst can more than treble the lifetime of corrugated boxes under cycling humidity conditions and a steady load. [36]

HCL was used for the cellulose to be hydrolyzed more quickly. HCL affects the rate of hydrolysis in the sense that it increases it significantly. [37]

A.1.2.3. Waste paper substrates with surfactant agents

First, the blender was used to blend the dried cellulose with water. After blending, the solution was put on the sonicator. Where NaCl (that has already been mixed) and other reagents such as SDS, CA, and HCL were then added.

The preparation of NaCl was simple. Mix 2.922g of NaCl with 5mL of ionized water on the magnetic spinner and let everything stir for about 30min and then take it out and add to the solution in the sonicator for which it stayed mixing for about 45 minutes.

The following reagents were then prepared: CA - Citric acid; SDS - Sodium dodecyl sulfate; HCL - Hydrochloric acid. Originally, 0.015g of SDS was used and 0.25g CA was added. But eventually, the quantity of SDS added differed.

Before putting the solution in the oven, the mix was taken from the sonicator and put in a different magnetic mixer for another 40 minutes with 700 rpm and 21ª Celsius.

A.1.2.4. Morphology and properties of the recycled paper substrates

From the images of 3% cellulose and 1% cellulose, there is a significant change in texture. It is clear from **Figure A.1.3**, that recycled paper substrates with 3% are not as uniform. This cellulose was aged in the sense that the cellulose was taken and then put in water for a day and then analyzed.

From **Figure A.1.3**, it also appears that the paper with no reagents appears to be the best. It is the clearest and is structurally sound. (More SEM pictures in **Annex A.2.2**).

In the end, it was decided to use 0.5% as it was a good percentage and it turns out that compared with the other recycled paper substrates that were added reagents this was more uniform and had a good structure. 0.5% cellulose with different weights of SDS were also be made and analyzed.

In **Figure A.1.3** are recycled paper substrates with different weights of the reagent SDS. **Figure A.1.4** is a SEM picture of 0.5% Cellulose that has no reagents (Surface and Cross-section).

Figure A.1.3— Picture of 3 recycled paper substrates: The first recycled paper substrate was 1% Cellulose with 0.5g of CA and 0.15g SDS. The second recycled paper substrate is the one with no reagents and just water and cellulose. The third recycled paper substrate is the one with the same characteristics as the first recycled paper substrate but just aging

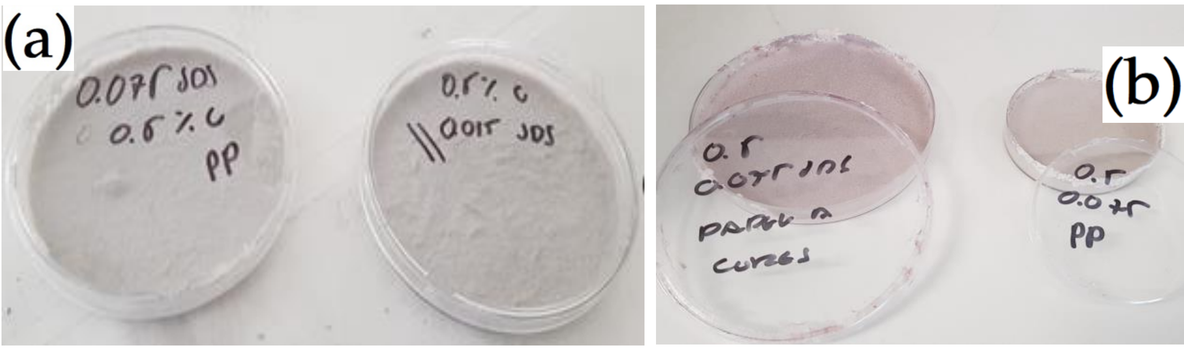


Figure A.1.4 — Picture of 4 recycled paper substrate s (a) First recycled paper substrate: 0.5% Cellulose; 0.0075g SDS. Second recycled paper substrate: 0.15g SDS; 0.0015g SDS (b) First recycled paper substrate: 0.5% cellulose; 0.0075g SDS but with paper obtained from the colored part from the newspaper

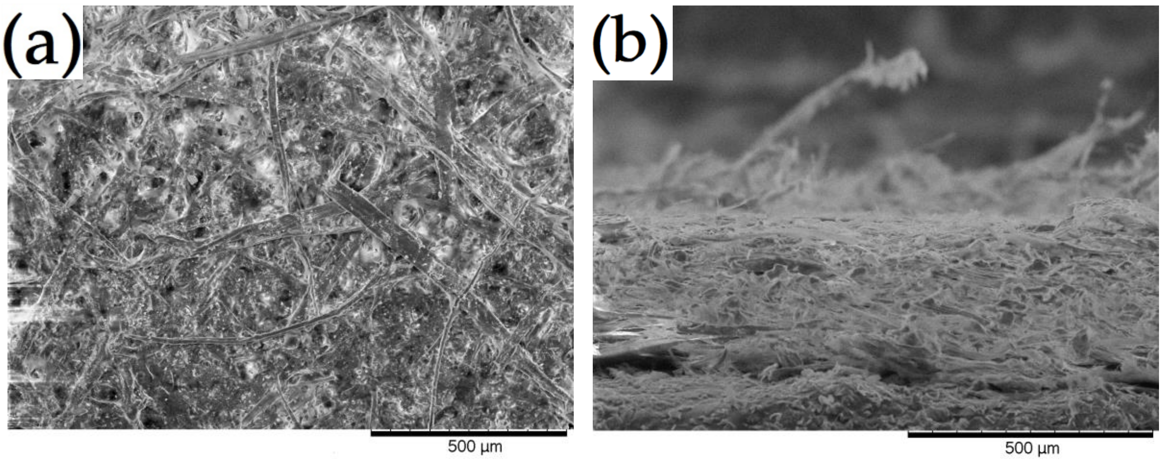


Figure A.1.5 — Pictures of SEM of 0.5% Cellulose "Pure" (No reagents) -
(a) Substrate surface (b) Cross-section

Table A.2 — Measurements and density and porosity of various recycled paper substrates with different cellulose and different methods used in the process

Recycled paper substrate	Thickness (mm)	Mass (g)	Volume (cm^3)	Density (g/cm^3)	Porosity (%)
Cellulose 1% w/Sonicator Thin film No blender	0.18	0.15	0.07	2.01	93
Cellulose 0.5% w/Sonicator 0.5g CA 0.075g SDS	0.08	0.08	0.03	2.54	98
Cellulose 0.5% w/Sonicator Thin Film No blender	0.08	0.09	0.03	3.03	98
Cellulose 0.5% Sonicator w/0.5g CA 0.015g SDS	0.08	0.10	0.03	2.88	98
Cellulose 0.5% "Pure" (No reagents) w/Sonicator	0.03	0.03	0.01	2.60	81
Cellulose 0.5% 0.5g CA 0.15g SDS Aged	0.11	0.12	0.04	2.61	83
Cellulose 0.5% Sonicator 0.5g CA 0.15g SDS	0.07	0.09	0.03	3.13	79
Cellulose 1% 0.5g CA 0.15g SDS without Sonicator	0.05	0.06	0.02	3.21	79

Note: Density of CA is: 1,66 $\frac{g}{cm^3}$ .Density of SDS is: 1,01 $\frac{g}{cm^3}$.

From **Table A.2**, some conclusion can be made.

The sonicator is very helpful in making sure that the cellulose and reagents are well mixed, but, the most important step is without a doubt the Blending process.

Recycled paper substrates without a blender were much worse than those that were blended. So blending is a must and the communication process helps but it is not necessarily fundamental as blending.

From the pictures and the values of thickness and porosity, it was decided that the recycled paper substrate with no reagents was the one that was going to be used.

Also, the recycled paper substrate with no reagents was the thinnest one and with least weight which also means the least amount of density.

In **Figure A.2** and **Figure A.3** are the equipment and regents used for the process mentioned previously. This equipment was also used for the fabrication of water and ethanol recycled paper substrates.

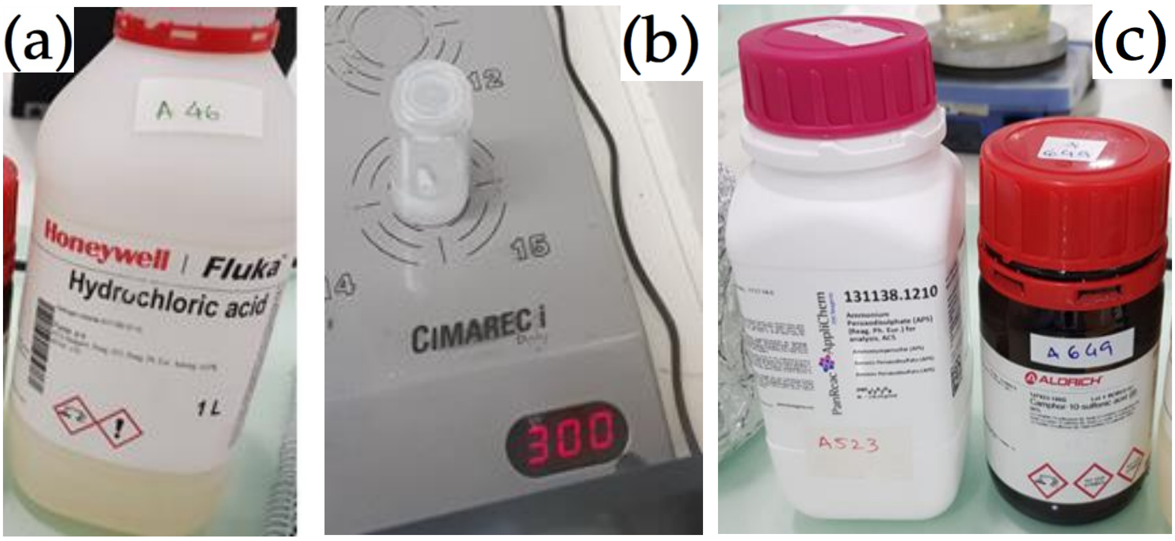


Figure A.2 — (a) Hydrochloric acid (b) NaCl being mixed with water (c) SDS and CA

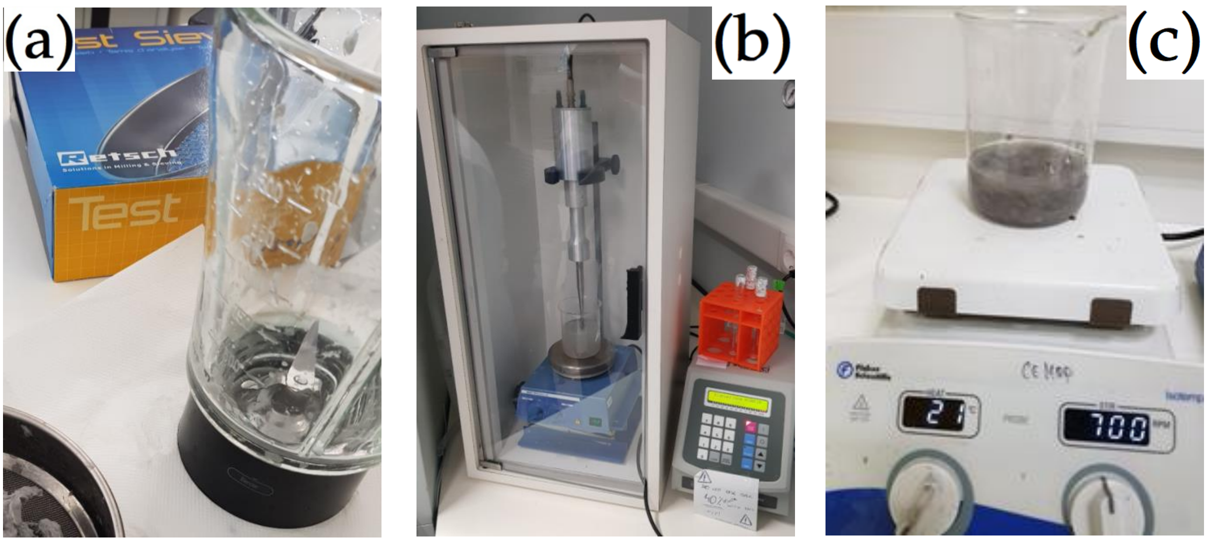


Figure A.3 - (a) Blender and filter used; (b) Sonicator (c) Magnetic agitator with solution being mixed at 21ªC with 700rpm

A.1.3. Dried Cellulose

In **Figure A.4** are the cellulose before being put in the oven and afterwards.

Figure A.4 — (a) End product after filtration and before putting it in the oven again (b) Dried cellulose

A.1.4. Filtration paper

In **Figure A.5** is shown the filtration paper before being used and after being used.
On the left, is the paper that is completely new and was used for the filtration process. On the right, is paper that was already used and that afterwards went into the oven for 24h to be able to reuse again.

Figure A.5 — Filtration paper used

A.1.5. Molds

Using molds was inefficient but was interesting to experiment and see what would happen to the recycled paper substrates if left to dry for 24h.

In **Figure A.6** are some of the molds used and the final results. As can be seen in the photos, the end product was not satisfactory and so it was best to scratch this idea and continue without molds.

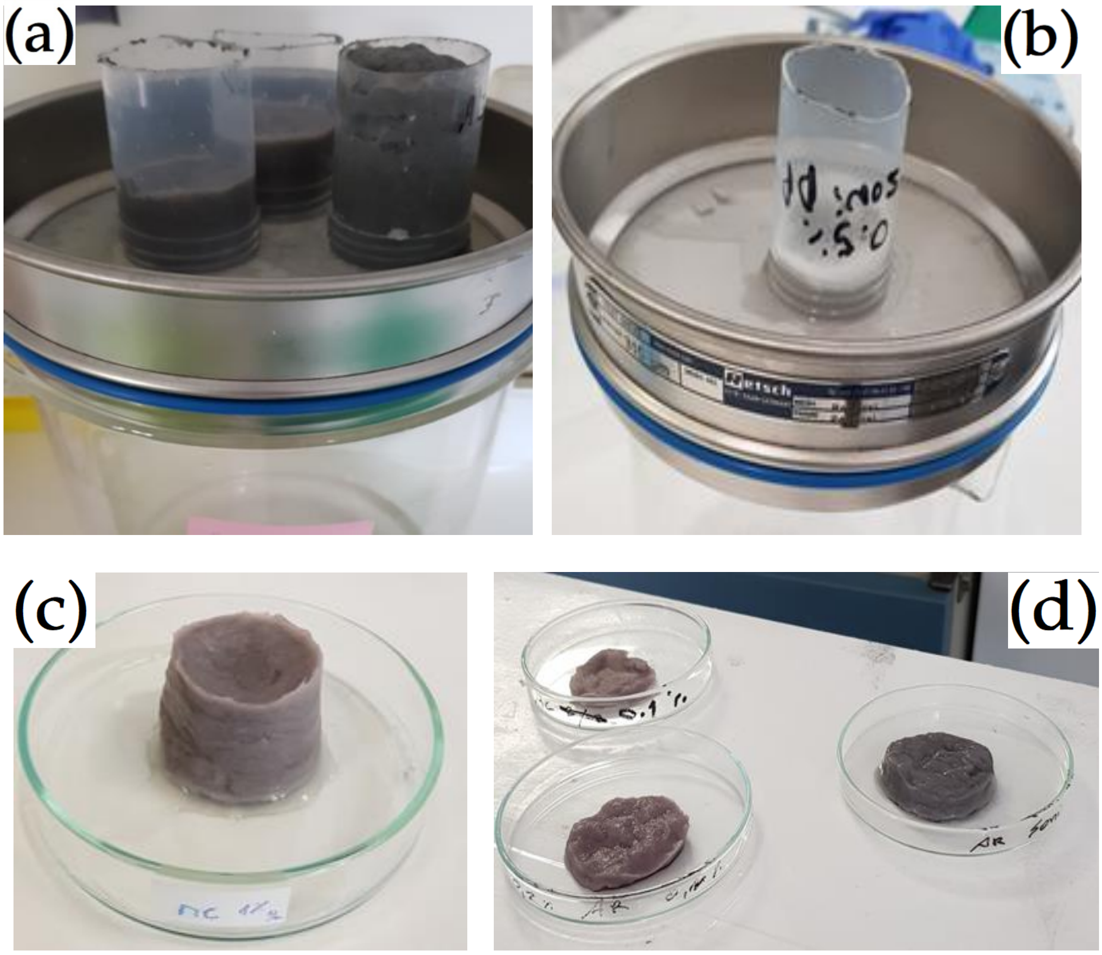


Figure A.6 — Molds that were left to dry for 24h with varying amounts of cellulose - (a) 3 molds with same circumference but different weights (b) Another mold with 0.5% Cellulose- (c) End result of the drying process through filtration after being taken from the mold and dried for 24h - 1% Cellulose with a mold of greater height (d) Other three molds after drying for 24h

A.1.6. pH levels and pH strips

For the reactions regarding SDS and the other regents, measurements of pH levels were made before and after introducing all the components of the reaction and after. This is to make sure that the reaction appears and also to check what the pH levels were.

Before the reaction, the strip was showing a greenish color which corresponds to a pH level of 7 and the second one appears as a pH level of 4. This means that the reaction occurred and everything was mixed well.

These strips were not used for the water and ethanol recycled paper substrates.

A.1.7. Functionalization with PPy

In the **Figure A.7** and **Figure A.8** are shown the recycled paper substrates being left to dry. These are the recycled paper substrates functionalized with PPy with the Dipping process.

Figure A.7 — Multiple recycled paper substrates with varying degrees of Ethanol being left to dry after functionalization with PPy.

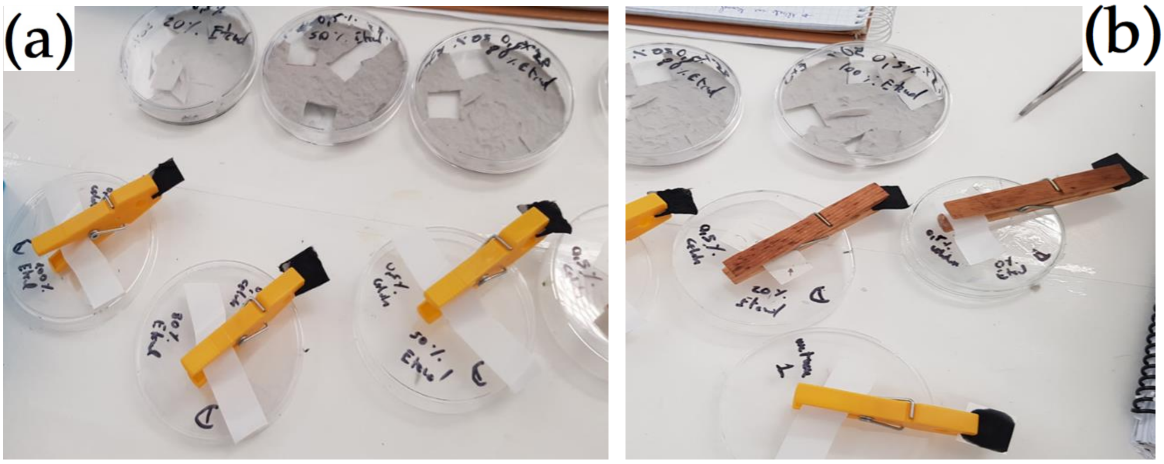


Figure A.8 — (a) (b) Photos of recycled paper substrates with: 20% Ethanol; 50% Ethanol%; 80% Ethanol that are being left to dry and their respective boxes contacting the paper used.

In **Figure A.9** are shown pictures related to the actual functionalization process. There are pictures of the two solutions used for Drop-cast and Dipping process and the re-cycled paper substrates functionalized for reference.

In **Figure A.10** and **Figure A.11** are drawings depicting the Drop-cast and Dipping process.

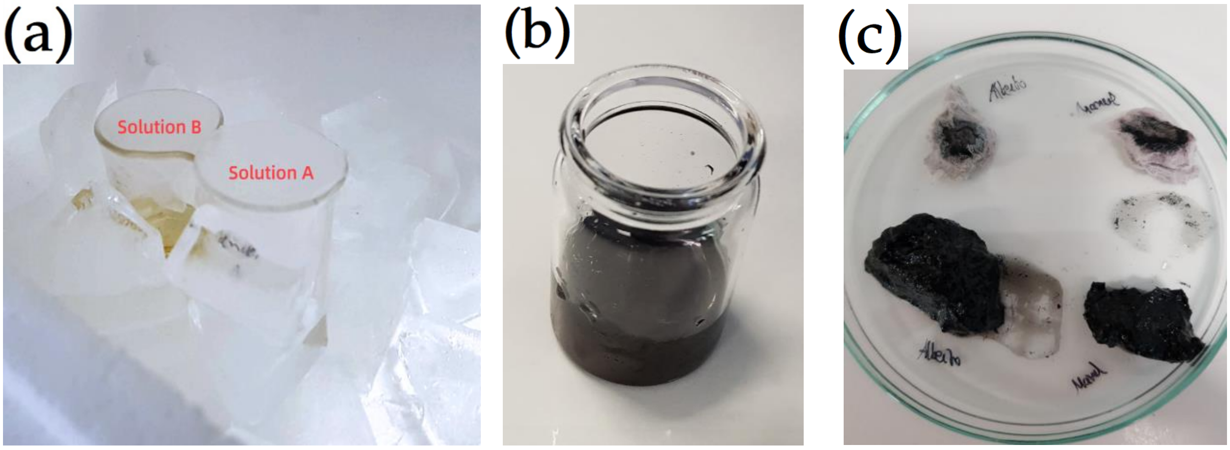


Figure A.9 — (a) Picture of both solutions in Ice. Solution B at the left showing a darker color while Solution A shows a clearer picture; (b) End result of mixing both solutions (This is the solution that was used for Drop-cast and Dipping); (c) Recycled paper substrates that were functionalized. At the top are two recycled paper substrates that were functionalized with Drop-cast. And at the bottom, two recycled paper substrates dipped in the solution (Dipping process)

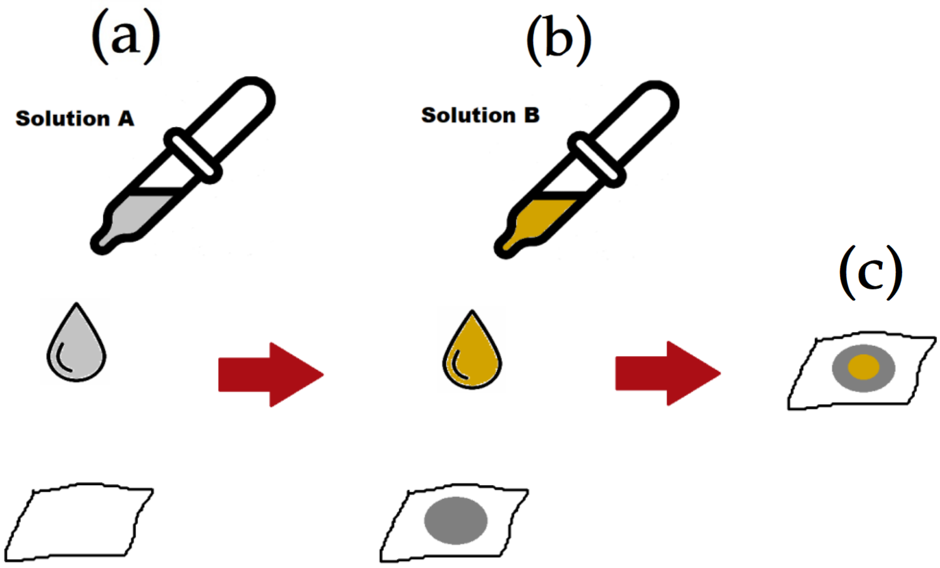


Figure A.10 — Drawing summarizing the Drop-cast method. (a) Dropping the solution A on the paper. (b) Dropping solution B on the paper; (c) End result: Recycled paper substrates with solution B being on top and solution A

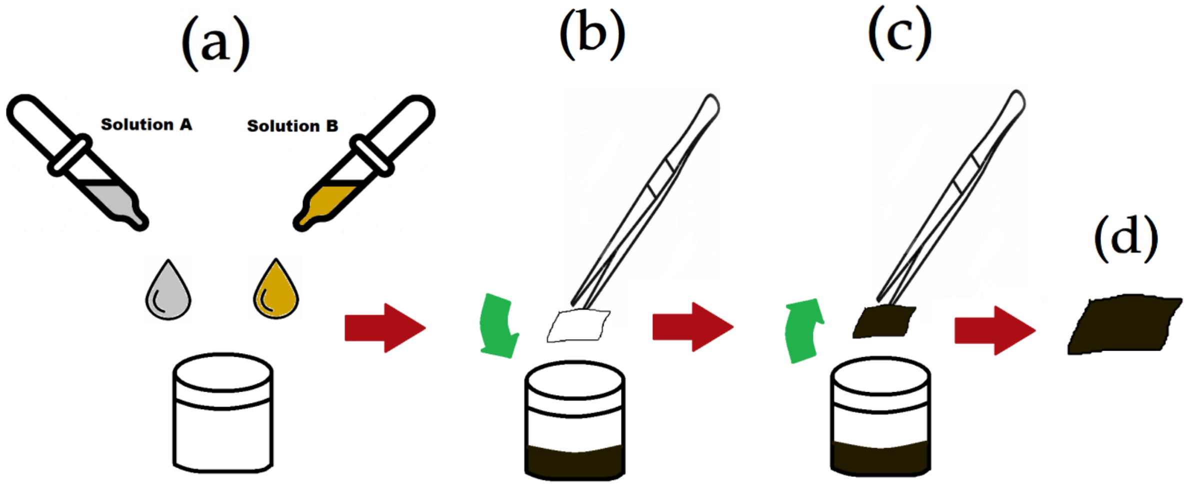


Figure A.11 — Drawing summarizing the Dipping process. (a) Mixing solution A and solution B to obtain the solution that was used for dipping the paper. (b) Using tweezers, the paper is picked up and dipped until it turns completely black (This process usually only takes a couple of seconds). (c) Removing the recycled paper substrate out (d) Dipped recycled paper substrate

A.1.8. Screen printing

Below are pictures that were taken during the Screen printing process (Shown in **Figure A.12**). The whole process lasted about 2h. Coal and Silver paint were used.

Whatman paper was used and laid on the bottom of the mold. 12 recycled paper substrates were obtained (Shown in **Figure A.13**) which were then cut into small pieces for making the device.

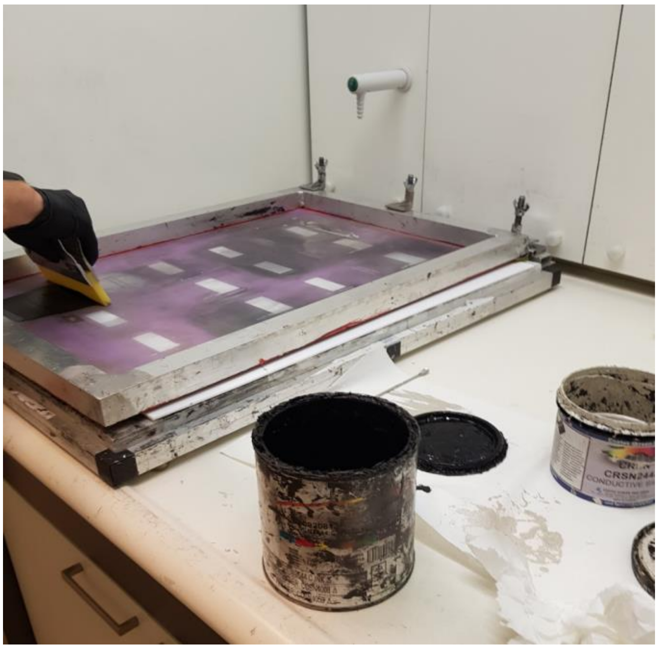


Figure A.12— Screen Printing process done in the FunPaper lab in Cemop - FCT/NOVA. Black paint corresponds to coal and silver paint corresponds to silver

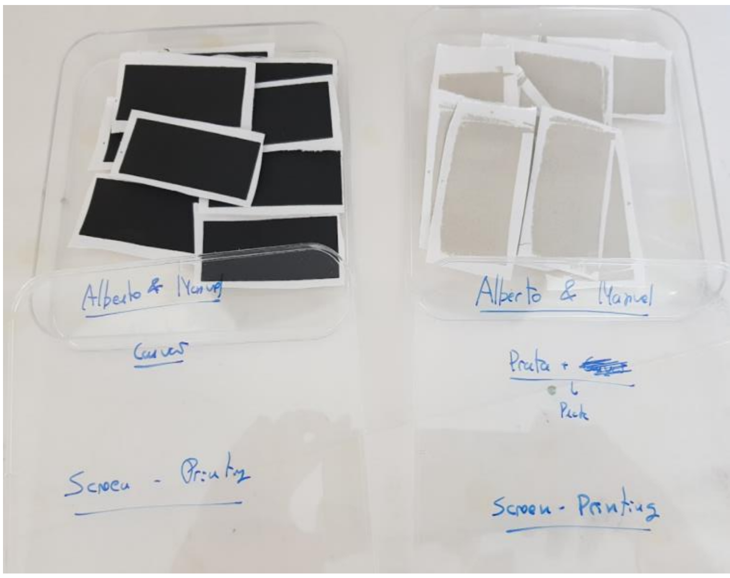


Figure A.13 — Picture of the final paper obtained through the Screen Printing process. The left ones are of Coal and the right one is of Silver

A.2. Chemical and Morphology Analyses

A.2.1. SEM and EDS Equipment

The SEM equipment used for the analysis was a SEM TM3030 model from the company Hitachi (Shown in **Figure A.14**).

Attached to it are an EDS equipment and a computer (connected to the whole SEM-EDS equipment was for obtaining and saving the pictures).

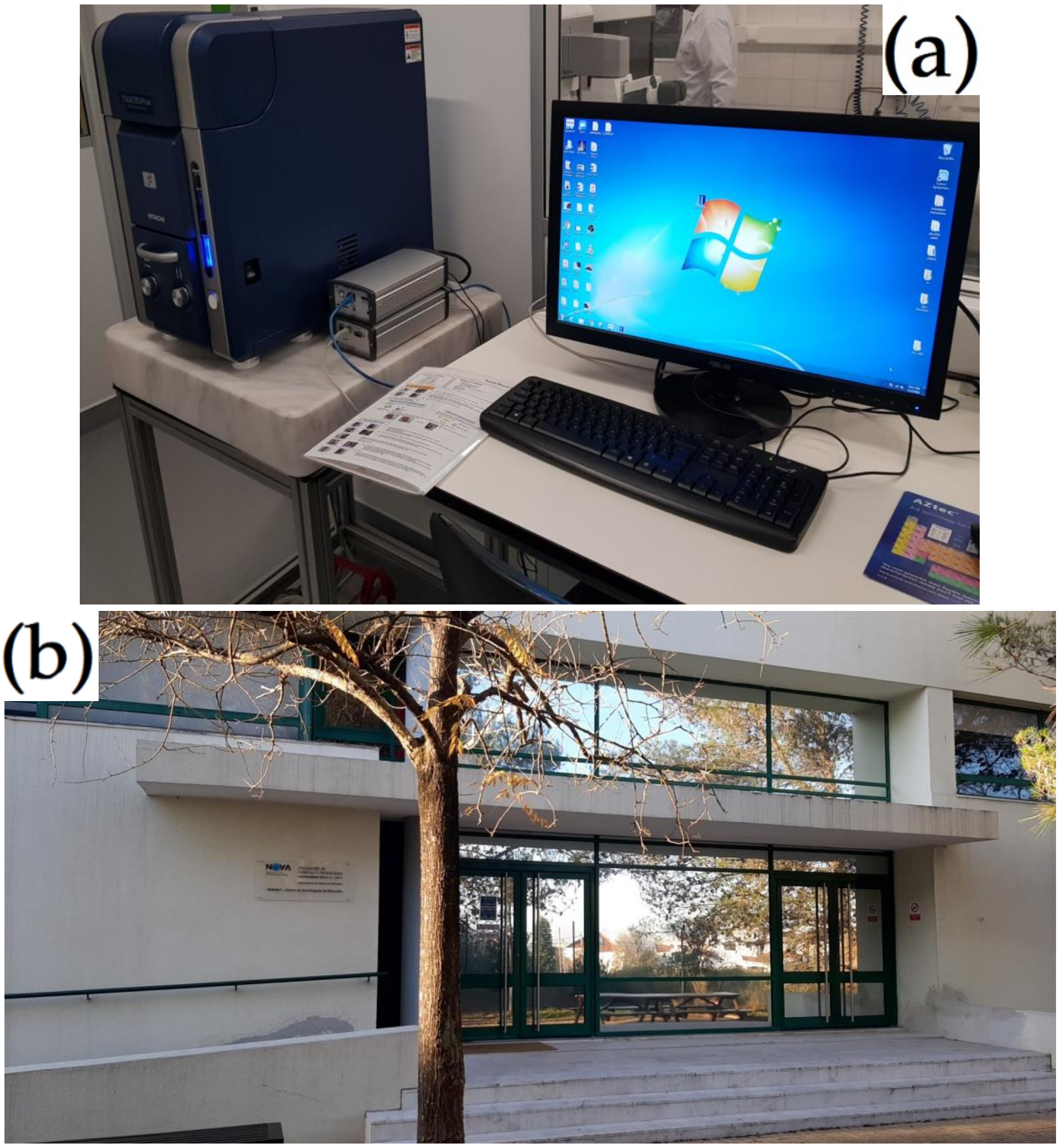


Figure A.14 — (a) Photo of Hitachi TM3030Plus used for SEM and EDS (Found at CENIMAT - FCT/NOVA) (b) Photo of Cenimat building where the SEM and FTIR equipment can be found

A.2.2. SEM – Varying Cellulose weights and varying SDS concentration

From **Figure A.15 to Figure A.22** are the SEM images obtained after obtaining cellulose recycled paper substrates with varying levels of cellulose and SDS. This was all done before moving on to the cellulose and water recycled paper substrates.

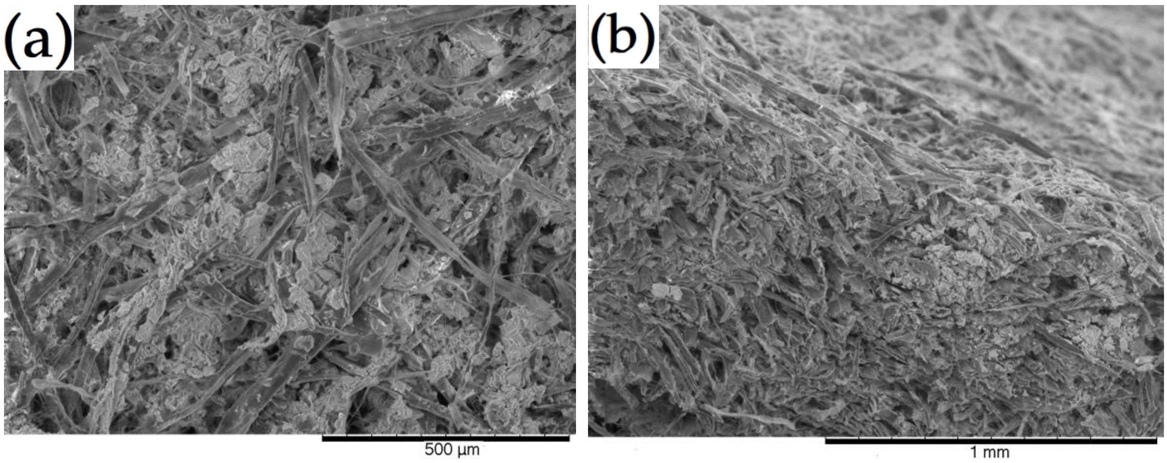


Figure A.15 — SEM Picture - 1% Cellulose in thin film mode -
(a) Substrate surface (b) Cross-section

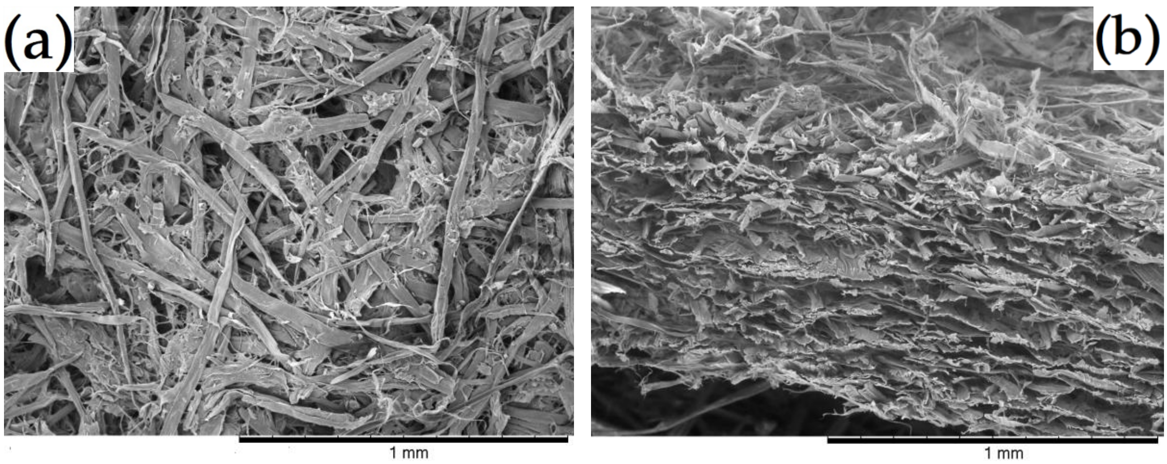


Figure A.16 — SEM picture – 3% Cellulose – (a) Substrate surface (b) Cross-section

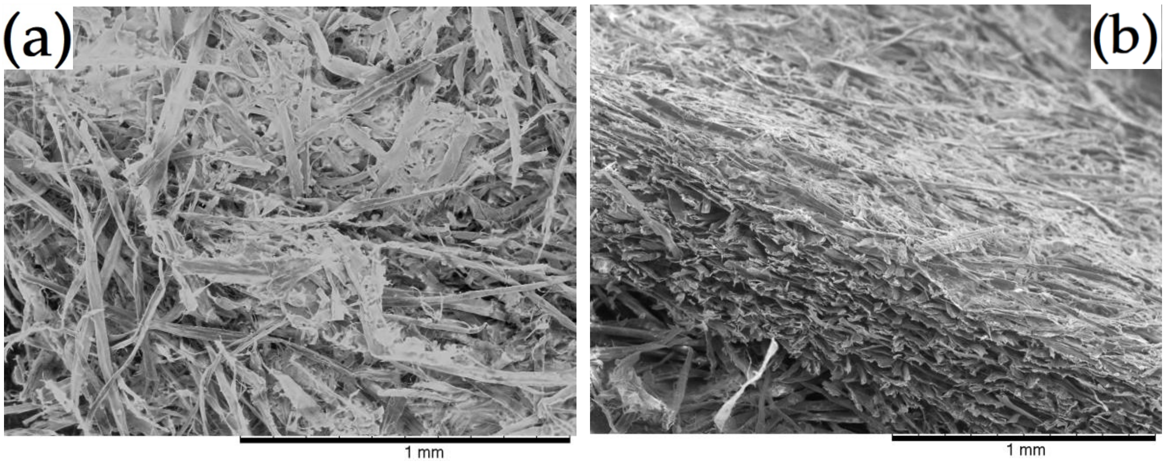


Figure A.17 — SEM picture - 1% Cellulose – (a) Substrate surface (b) Cross-section

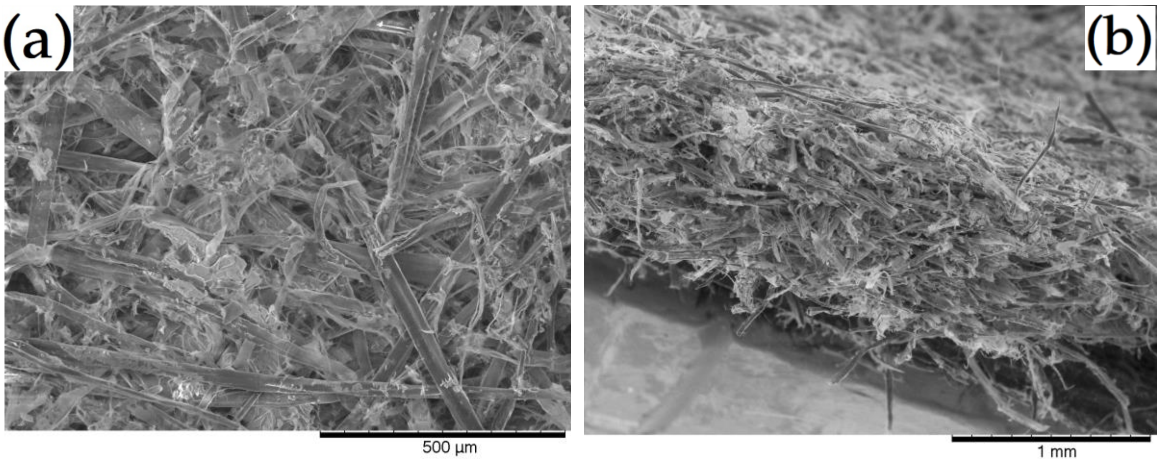


Figure A.18 — SEM picture – 0.2% Cellulose – (a) Substrate surface (b) Cross-section

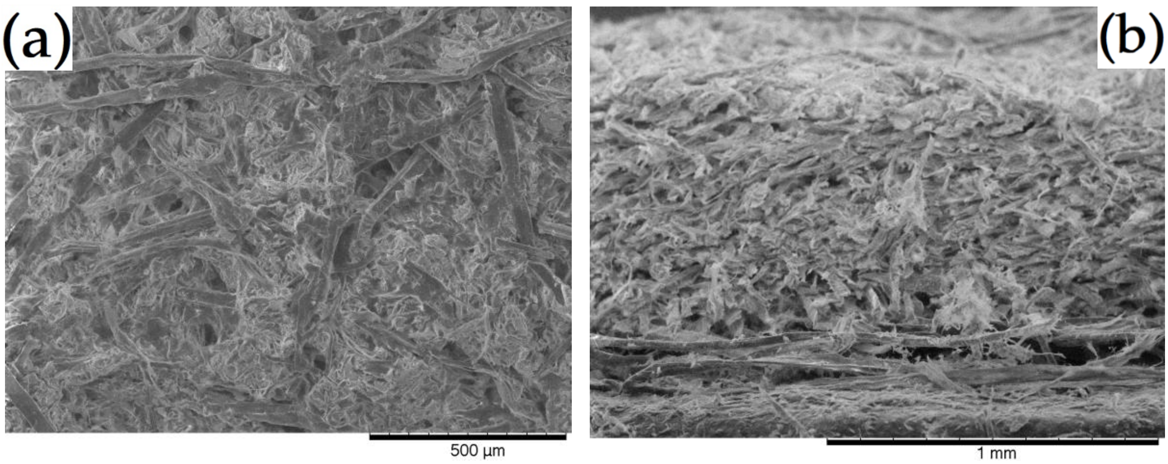


Figure A.19 — Picture of SEM – 0.5% Cellulose that was aged – (a) Substrate surface (b) Cross-section

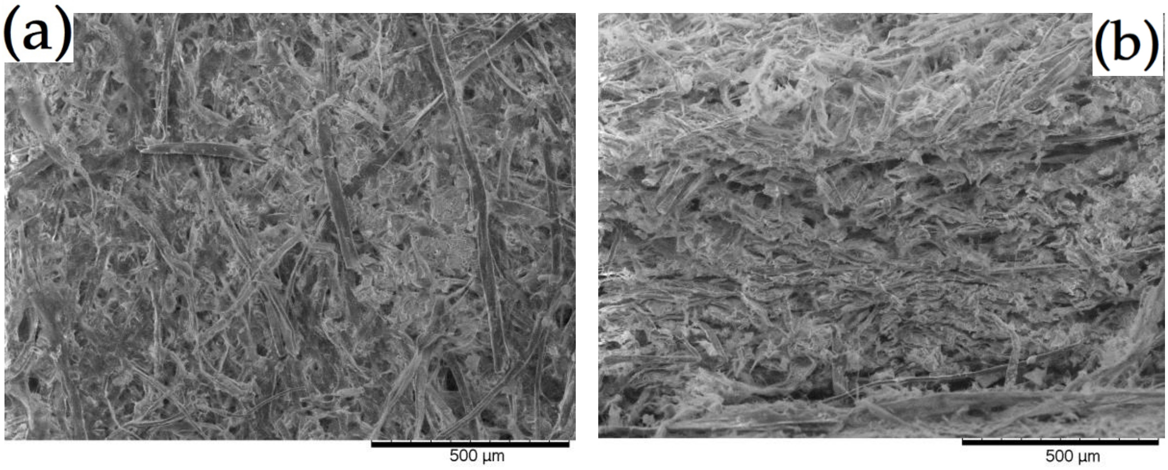


Figure A.20 — SEM picture – 0.5% Cellulose with 0.015g SDS – (a) Substrate surface (b) Cross-section

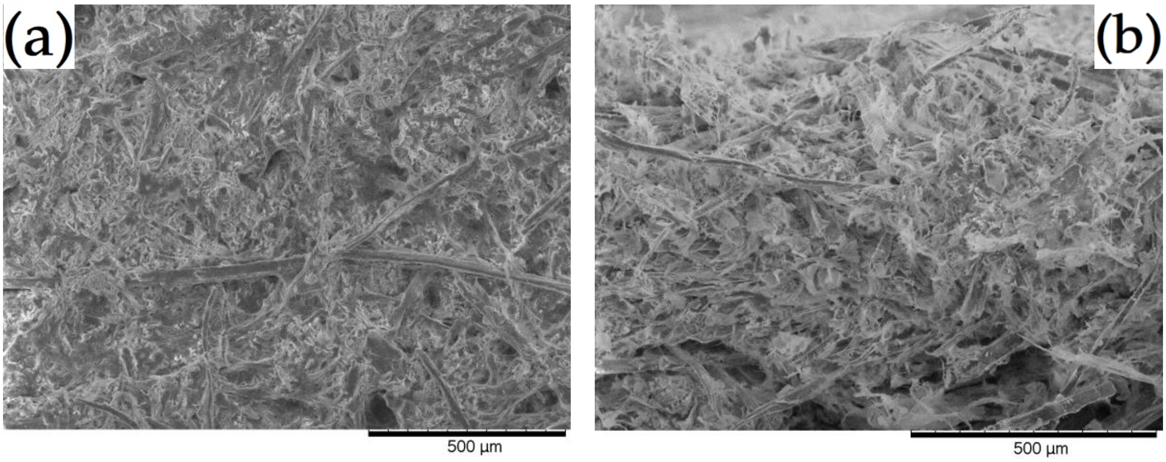


Figure A.21 — SEM picture - 0.5% Cellulose with 0.15g SDS – (a) Substrate surface (b) Cross-section

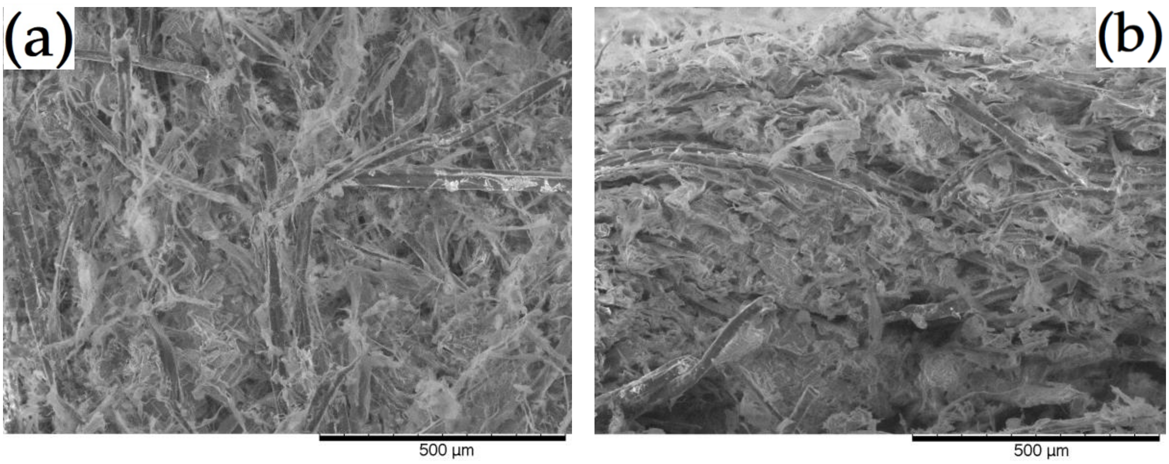


Figure A.22 — SEM picture – 0.5% Cellulose with 0.075g SDS – (a) Substrate surface (b) Cross-section

A.2.3. SEM - Second images related to EDS analysis of water and cellulose recycled paper substrates

These are the images related to when doing SEM-EDS analysis of water and cellulose recycled paper substrates. In order obtain a full EDS analysis it is necessary to first produce a SEM image.

From **Figure A.23** to **Figure A.26** are SEM images of the cellulose recycled paper substrates from 0% water and 100% Ethanol to 80% water and 20% Ethanol.

The picture of 0.5% Cellulose with 100% water and 0% Ethanol is found in the main thesis in **Figure 3.3.**

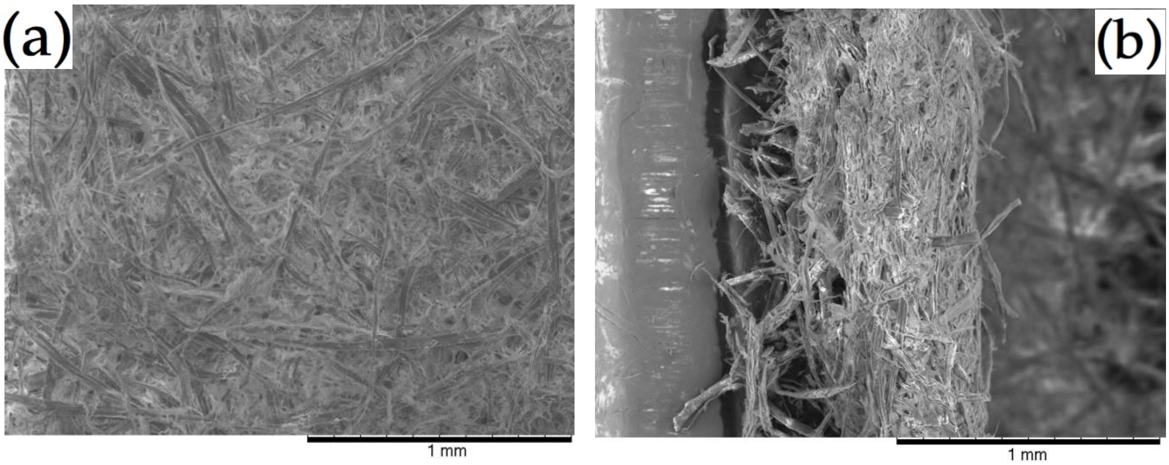


Figure A.23 – SEM - 0.5% Cellulose with 0% water and 100% Ethanol -
(a) Substrate surface (b) Cross-section

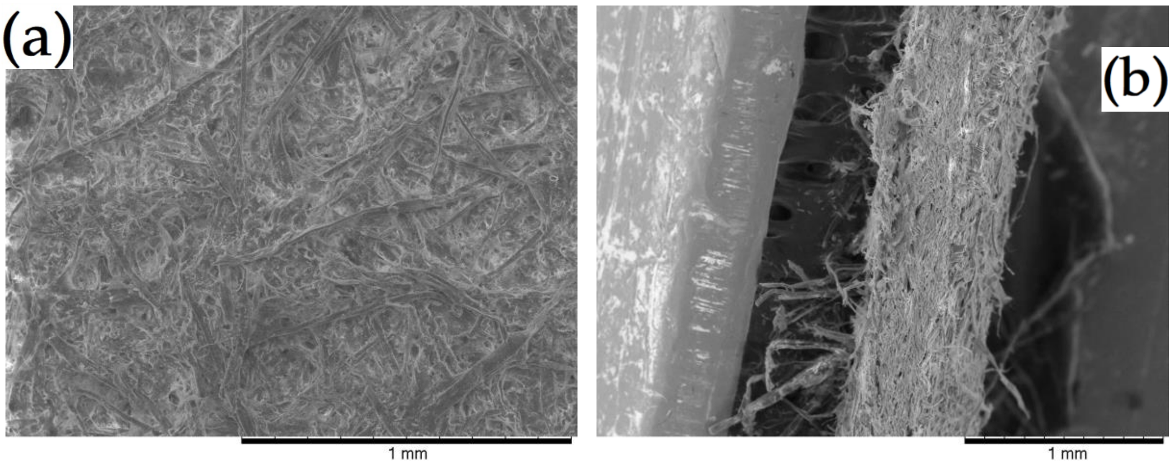


Figure A.24 – SEM - 0.5% Cellulose with 20% water and 80% Ethanol -
(a) Substrate surface (b) Cross-section

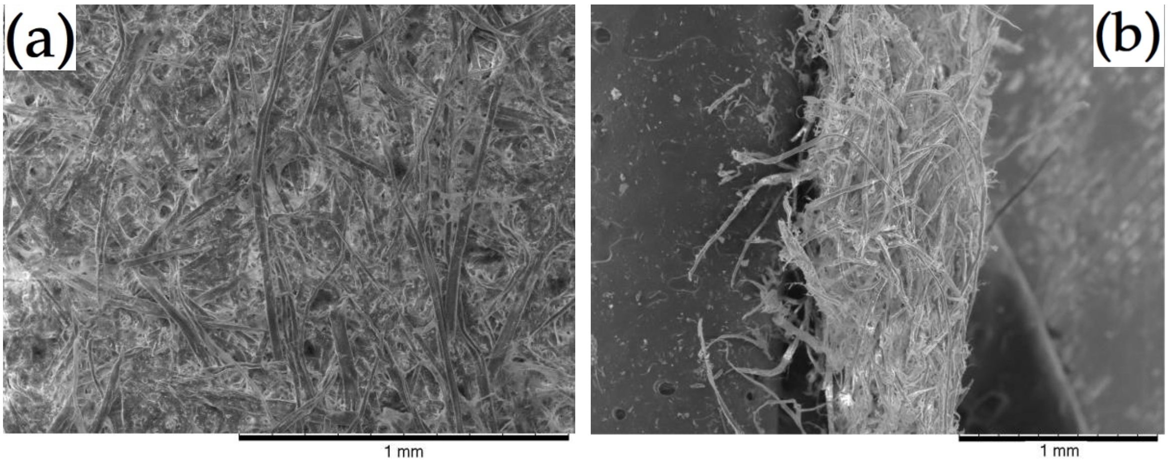


Figure A.25 – SEM - 0.5% Cellulose with 50% water and 50% Ethanol - (a) Substrate surface (b) Cross-section

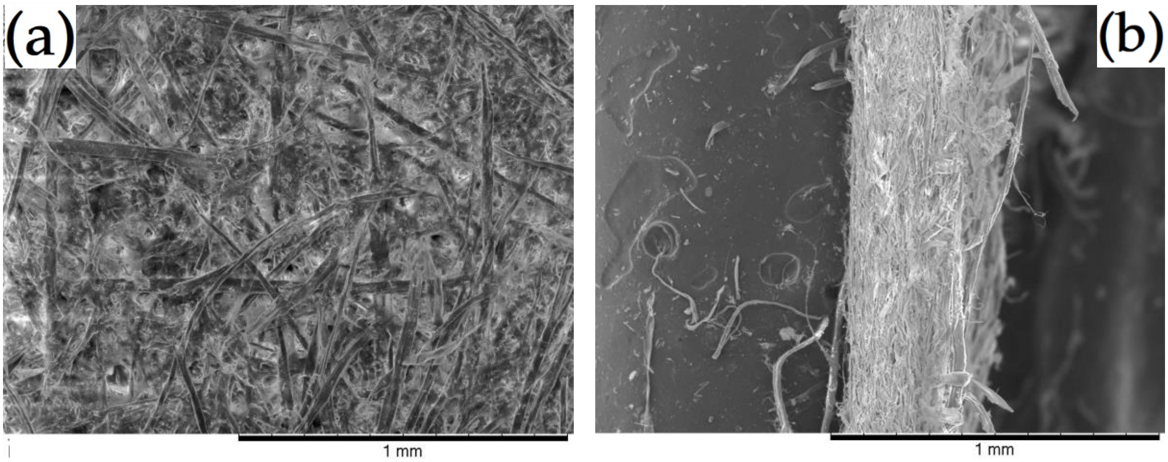


Figure A.26 – SEM - 0.5% Cellulose with 80% water and 20% Ethanol - (a) Substrate surface (b) Cross-section

A.2.4. SEM - Recycled paper substrates functionalized – Dipping and Drop-cast of water and ethanol recycled paper substrates

Figure A.27 to **Figure A.32** are other images taken after the functionalization of the water and ethanol recycled paper substrates.

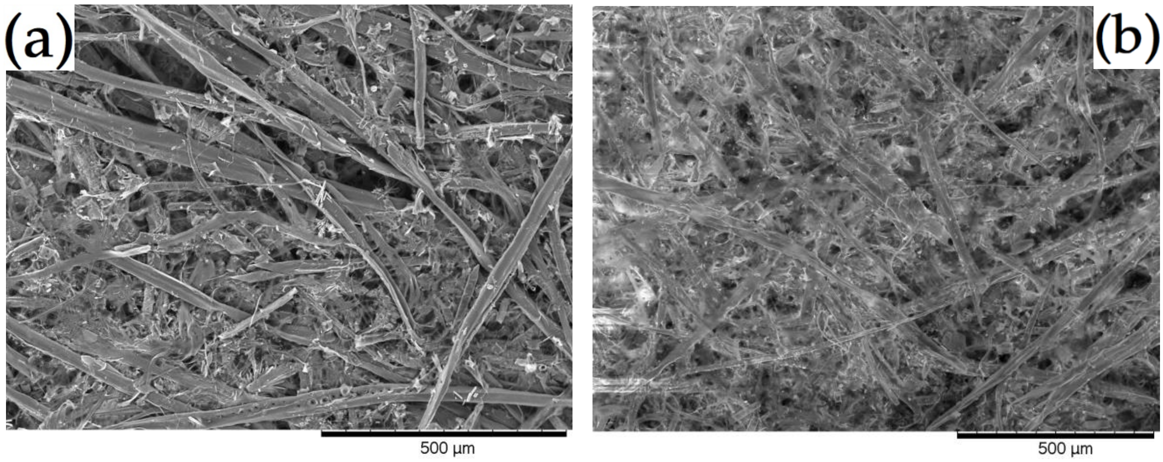


Figure A.27 — SEM picture - 0% Ethanol functionalized with PPy -
(a) Substrate surface (b) Cross-section

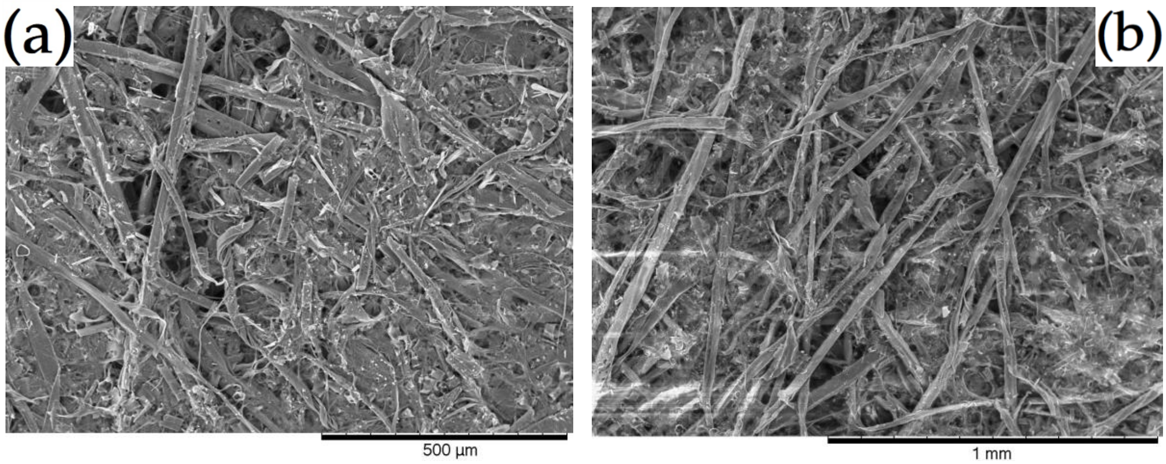


Figure A.28 — SEM picture - 20% Ethanol functionalized with PPy -
(a) Substrate surface (b) Cross-section

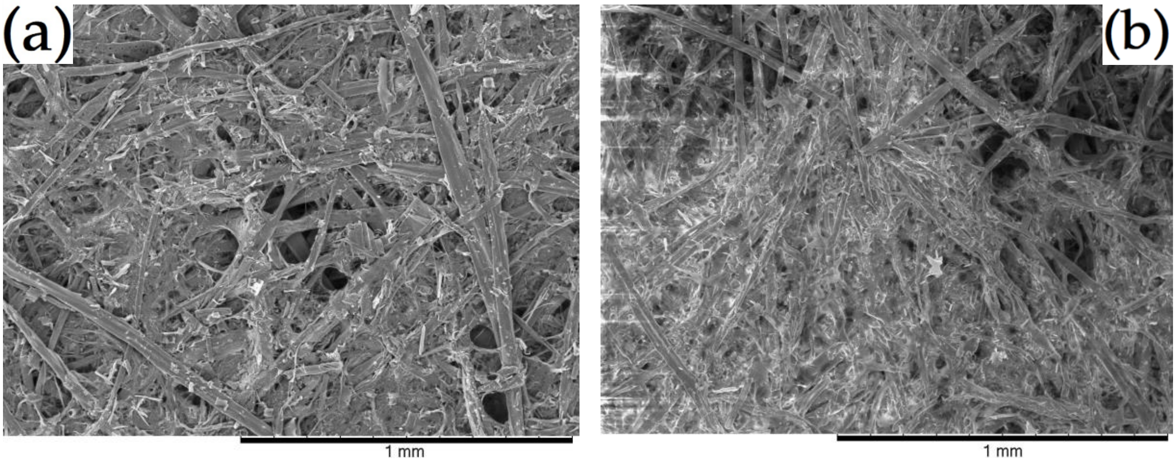


Figure A.29 — SEM picture - 50% Ethanol functionalized with PPy -
(a) Substrate surface (b) Cross-section

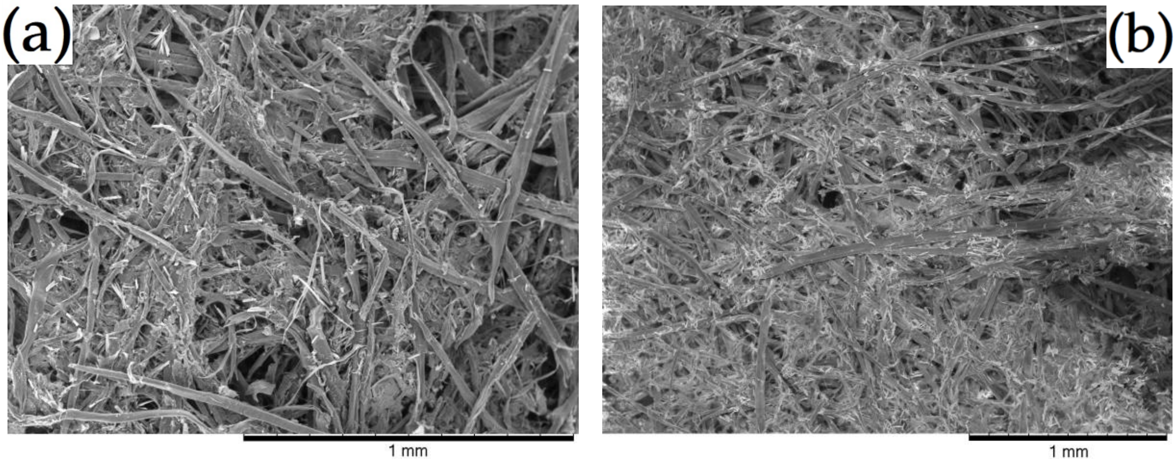


Figure A.30 — SEM picture - 80% Ethanol functionalized with PPy -
(a) Substrate surface (b) Cross-section

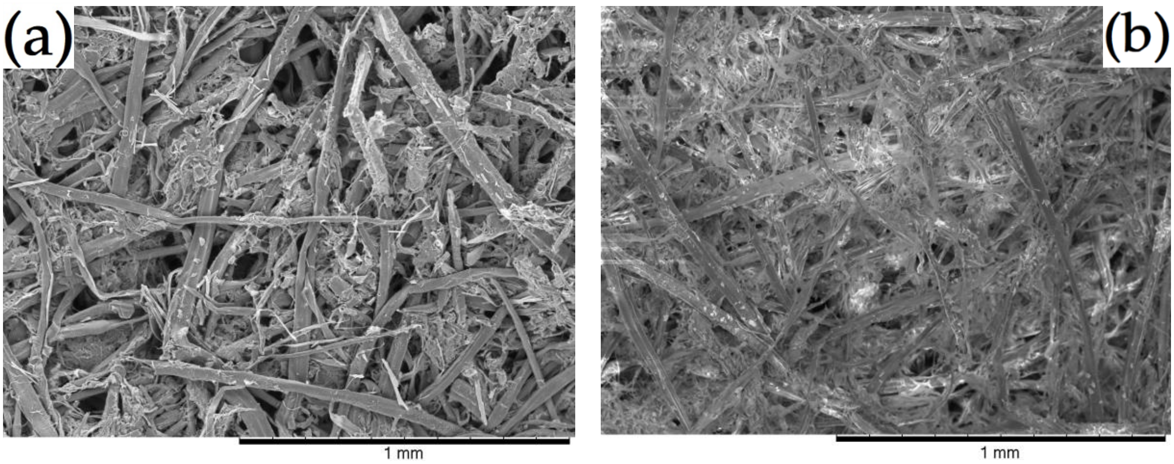


Figure A.31 — SEM picture - 100% Ethanol functionalized with PPy -
(a) Substrate surface (b) Cross-section

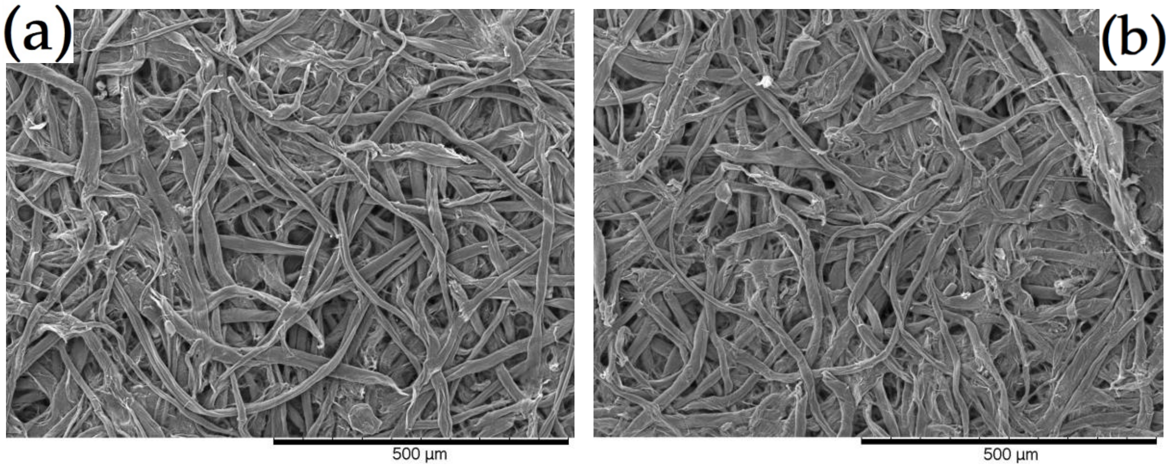


Figure A.32 — Whatman functionalized with PPy -
(a) Substrate surface (b) Cross-section

The table below (which corresponded to 50% Ethanol with the Dipping process) is an example of what was obtained with EDS analysis. The table was unaltered from the Word document that was obtained from the computer where EDS analysis was performed. This is just an example as displaying all tables in this format would take dozens of pages.

Element	AN	Series	Net	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]
Oxygen	8	K-series	3853	58.97	56.02	53.55
Carbon	6	K-series	1363	33.62	31.94	40.67
Sulfur	16	K-series	4615	12.04	11.44	5.45
Silicon	14	K-series	97	0.25	0.23	0.13
Aluminium	13	K-series	68	0.19	0.18	0.10
Magnesium	12	K-series	38	0.13	0.12	0.08
Calcium	20	K-series	17	0.07	0.07	0.03
			Total:	105.26	100.00	100.00

A.2.5. FTIR – More Absorbance graphs and of all and singular recycled paper substrates and values from Water and Ethanol recycled paper substrates not functionalized

All the analyses are of the Absorbance of the recycled paper substrates that were not yet functionalized (All presented in graph and of its singular graphs). The software used to obtain these graphics was **EssentialFTIR**. **Figure A.33** and **Figure A.34** are of all the recycled paper substrates together.

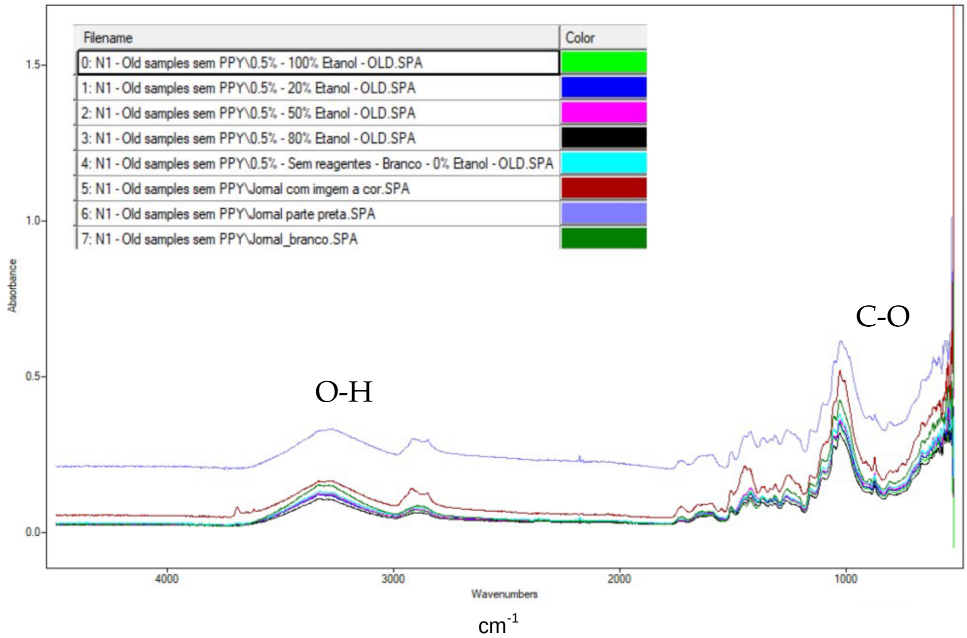


Figure A.33 — FTIR analysis of all recycled paper substrates including paper from newspaper used (Not functionalized) - Overlay mode

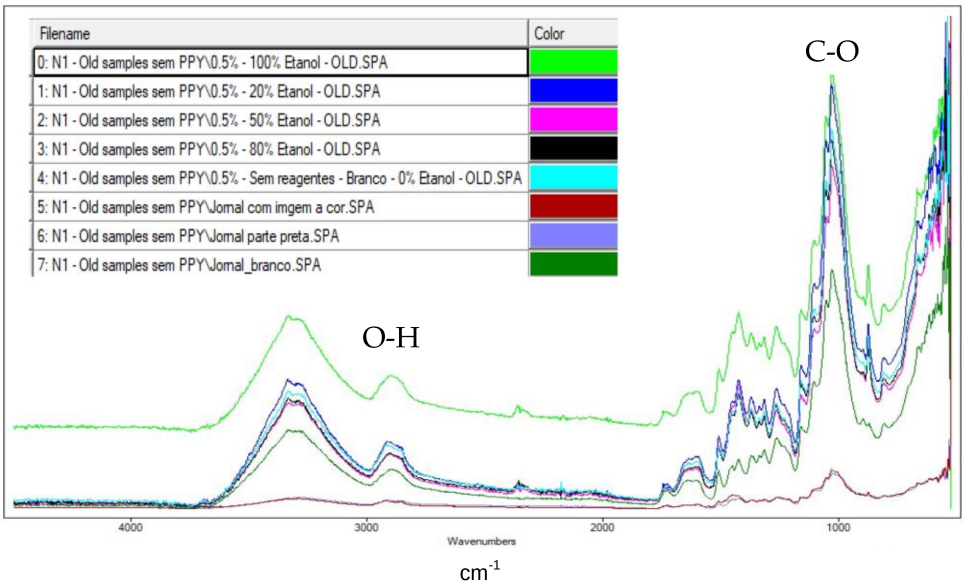
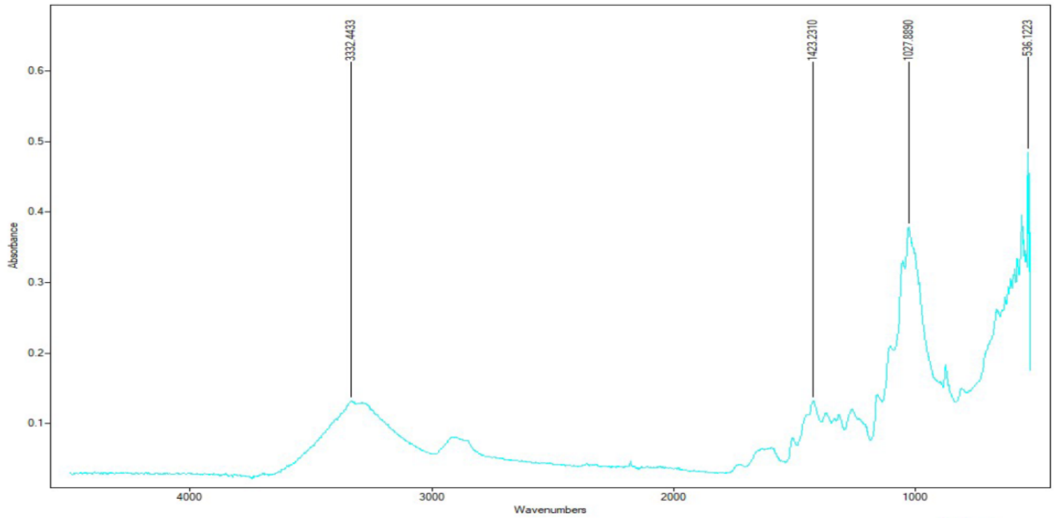


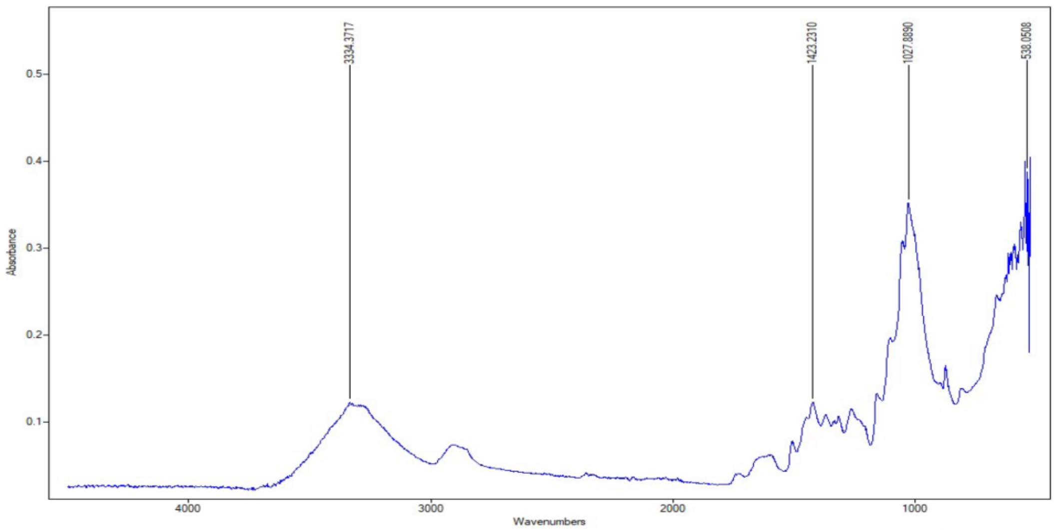
Figure A.34 — FTIR analysis of all recycled paper substrates including paper from newspaper used (Not functionalized) - Superimpose mode

The following images (**Figure A.35** to **Figure A.54**) were obtained from FTIR but singled out. Also, after the images is a table with peak values. The FTIR images displayed in the main section of FTIR were all these singulars added up. These figures are related to recycled paper substrates before functionalization and white, black and colored newspaper.



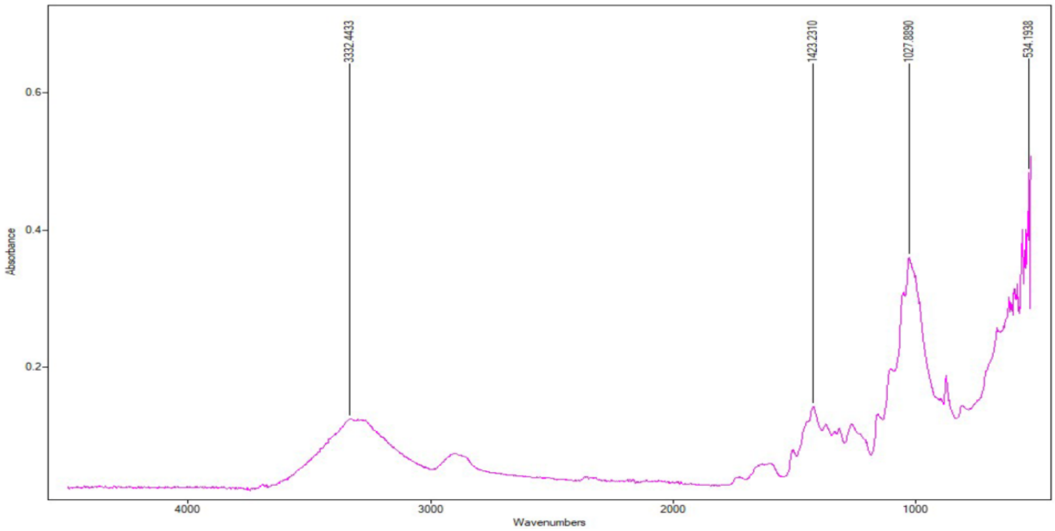
3332.4433 cm-1	1423.2310 cm-1	1027.8890 cm-1	536.1223 cm-1

Figure A.35 — FTIR Image - 0% Ethanol – FTIR spectrum and table of Peak values – Not functionalized



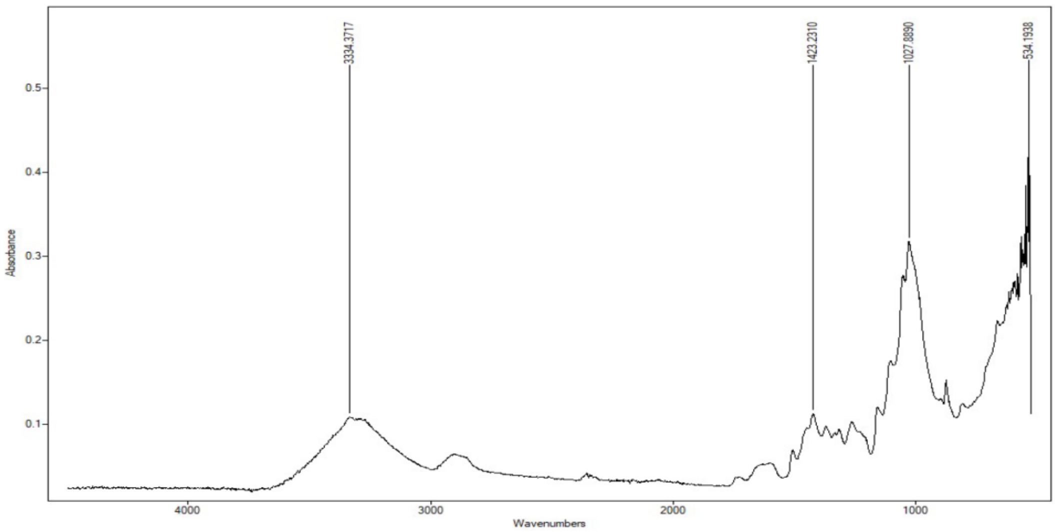
3334.3717 cm-1	1423.2310 cm-1	1027.8890 cm-1	538.0508 cm-1

Figure A.36 – FTIR Image - 20% Ethanol – FTIR spectrum and table of Peak values – Not functionalized



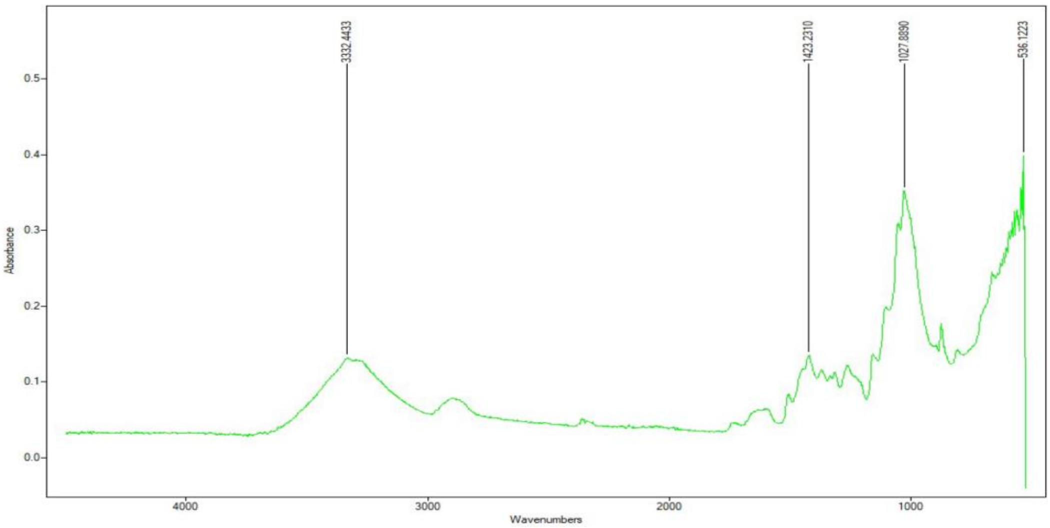
3332.4433 cm-1	1423.2310 cm-1	1027.8890 cm-1	534.1938 cm-1

Figure A.37 — FTIR Image - 50% Ethanol – FTIR spectrum and table of Peak values – Not functionalized



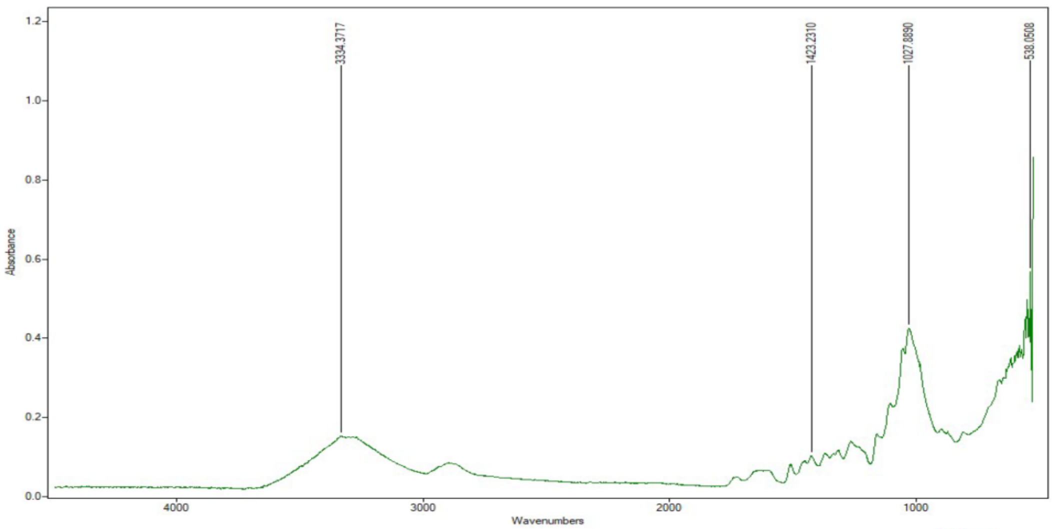
3334.3717 cm-1	1423.2310 cm-1	1027.8890 cm-1	534.1938 cm-1

Figure A.38 — FTIR Image - 80% Ethanol – FTIR spectrum and table of Peak values – Not functionalized



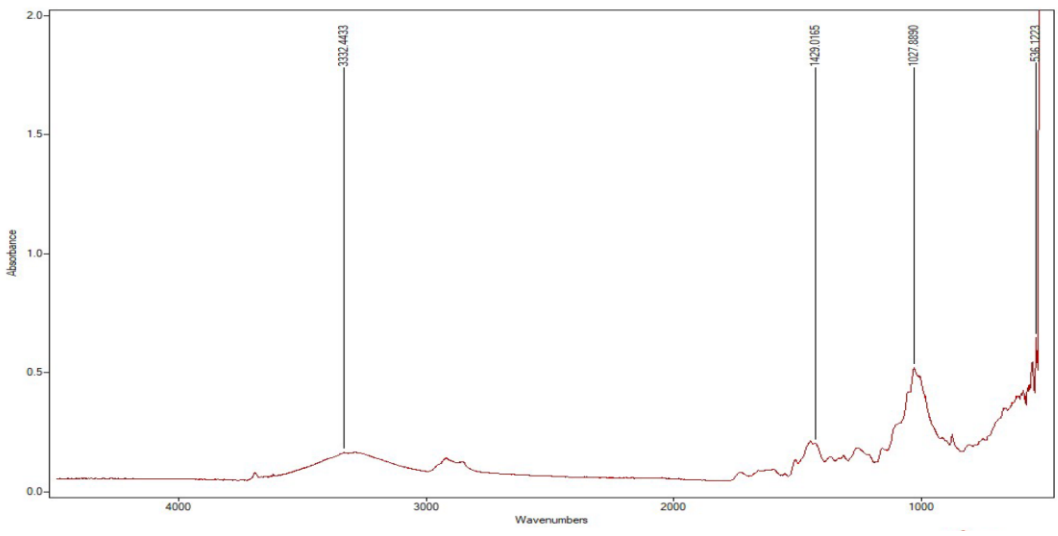
3332.4433 cm-1	1423.2310 cm-1	1027.8890 cm-1	536.1223 cm-1

Figure A.39 — FTIR Image - 100% Ethanol – FTIR spectrum and table of Peak values – Not functionalized



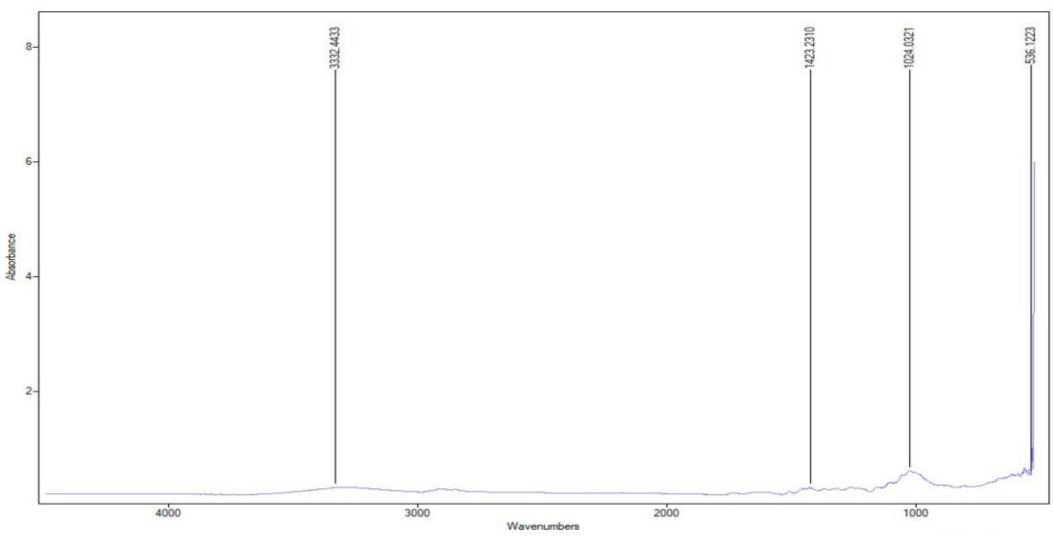
3334.3717 cm-1	1423.2310 cm-1	1027.8890 cm-1	538.0508 cm-1

Figure A.40 — FTIR Image - White paper – FTIR spectrum and table of Peak values – Not functionalized



3332.4433 cm-1	1429.0165 cm-1	1027.8890 cm-1	536.1223 cm-1

Figure A.41 — FTIR Image - Colored paper Ethanol – FTIR spectrum and table of Peak values – Not functionalized



3332.4433 cm-1	1423.2310 cm-1	1024.0321 cm-1	536.1223 cm-1

Figure A.42 — FTIR Image - Black paper obtained – FTIR spectrum and table of Peak values – Not functionalized

A.2.6. FTIR – Singular recycled paper substrates and values from Water and Ethanol recycled paper substrates (and Whatman Paper) functionalized with PPy - Dipping and Drop-cast

All the analysis below is of the Absorbance of the recycled paper substrates that were functionalized with PPy (All presented in graph and of its singular graphs). (**Figure A.43** and **Figure A.44**).

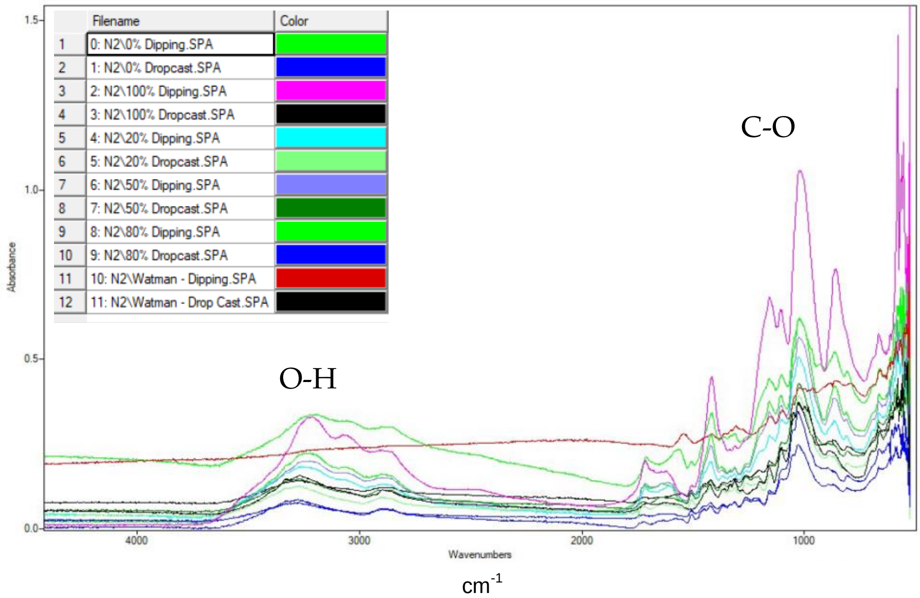


Figure A.43 — FTIR analysis of Recycled paper substrates of Ethanol and Whatman paper that went through the Dipping process and Drop-cast method with PPy – Overlay mode

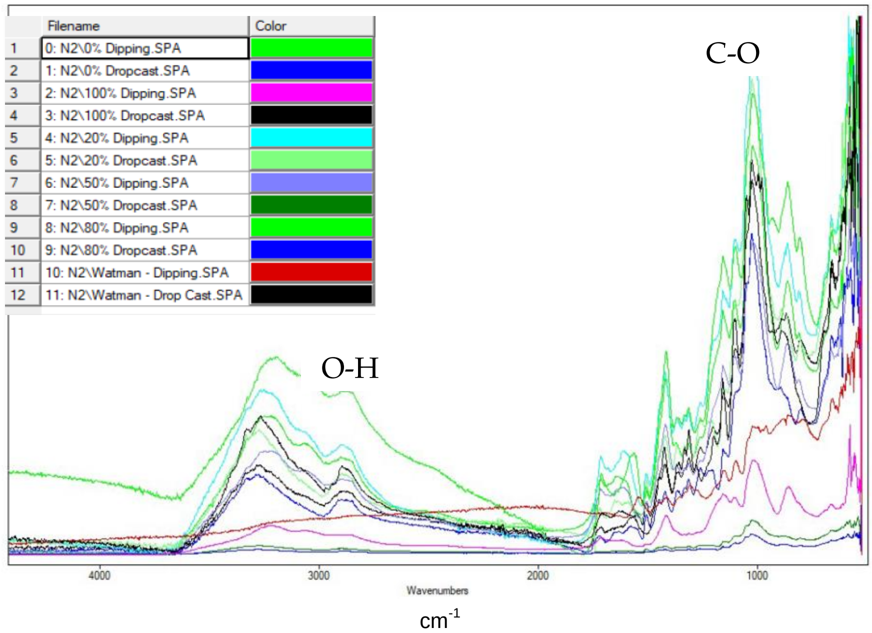
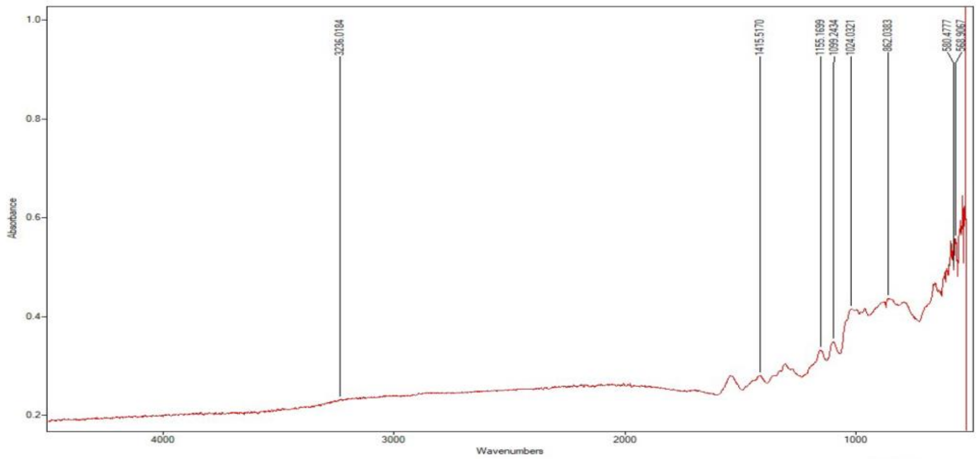


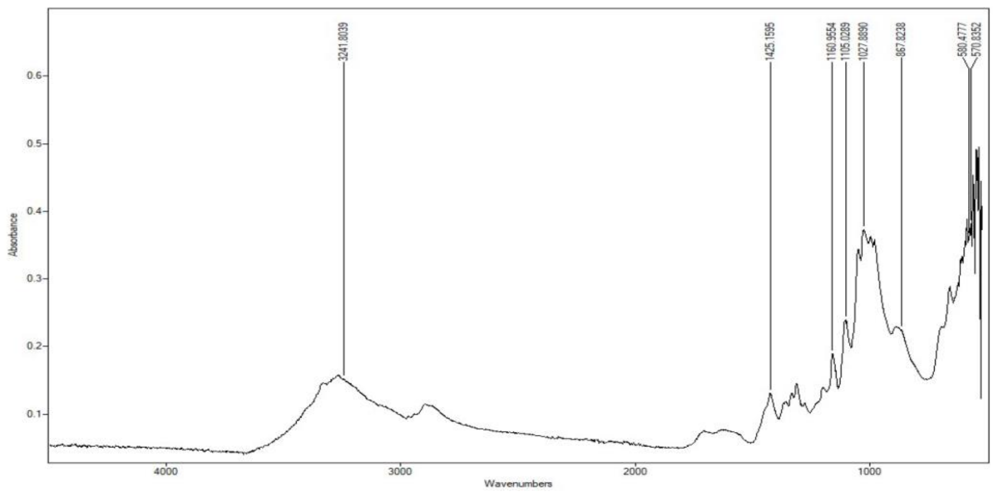
Figure A. 45 — FTIR analysis of Recycled paper substrates of Ethanol and Whatman paper that went through the Dipping process and Drop-cast method with PPy – Superimpose mode

The following images (**Figure A.45** to **Figure A.56)** were also obtained from FTIR but singled out with peak values. These figures are related to recycled paper substrates after functionalization with PPy (Dipping and Drop-cast).



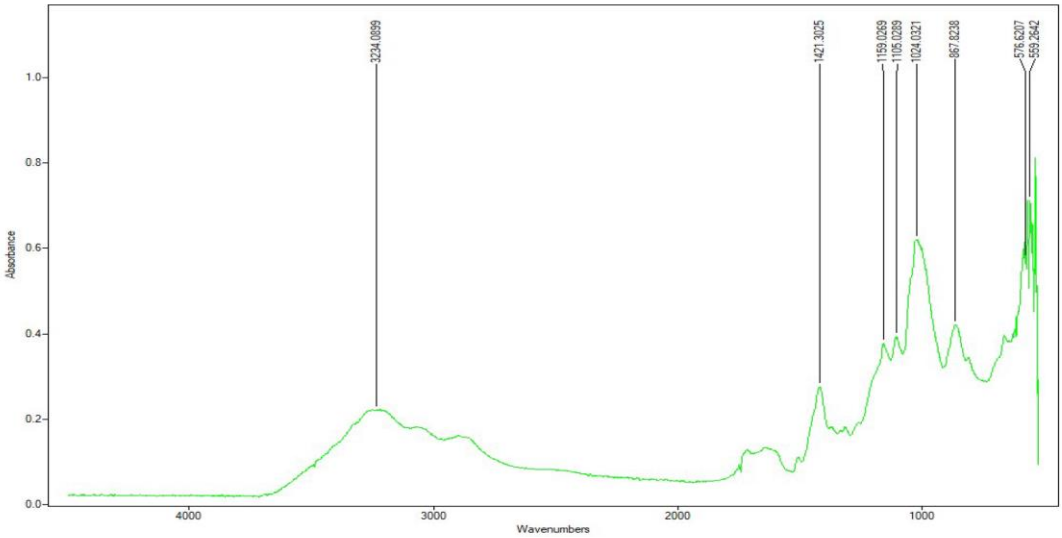
3236.0184 cm-1	1415.5170 cm-1	1155.1699 cm-1	1099.2434 cm-1	1024.0321 cm-1	862.0383 cm-1	580.477 cm-1	568.9067 cm-1

Figure A.45 — FTIR Image - Whatman paper - Dipping method - FTIR spectrum and table of Peak values – Functionalized with PPy



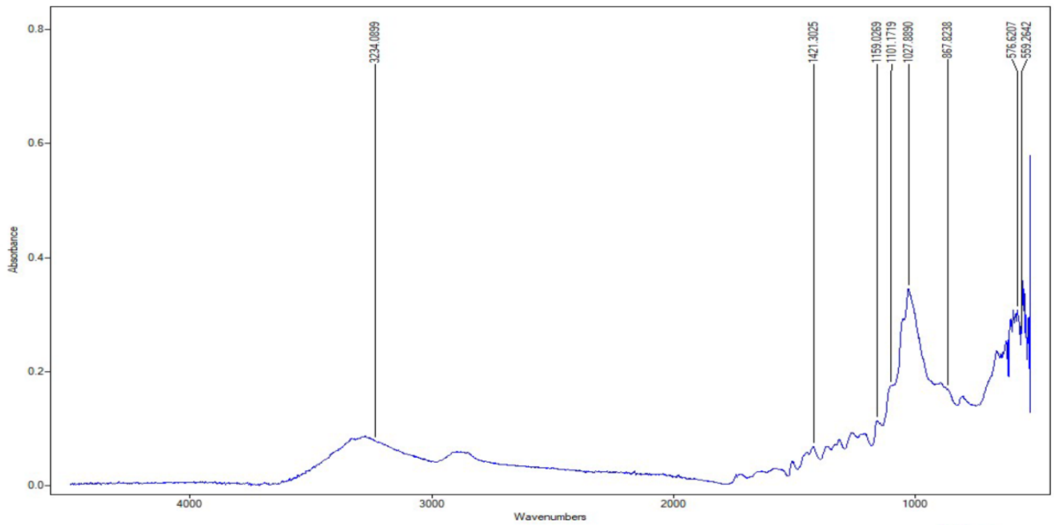
3241.8039 cm-1	1425.1595 cm-1	1160.9554 cm-1	1105.0289 cm-1	1027.8890 cm-1	867.8238 cm-1	580.4777 cm-1	570.8362 cm-1

Figure A.46 – FTIR Image - Whatman paper – Drop-cast method - FTIR spectrum and table of Peak values – Functionalized with PPy



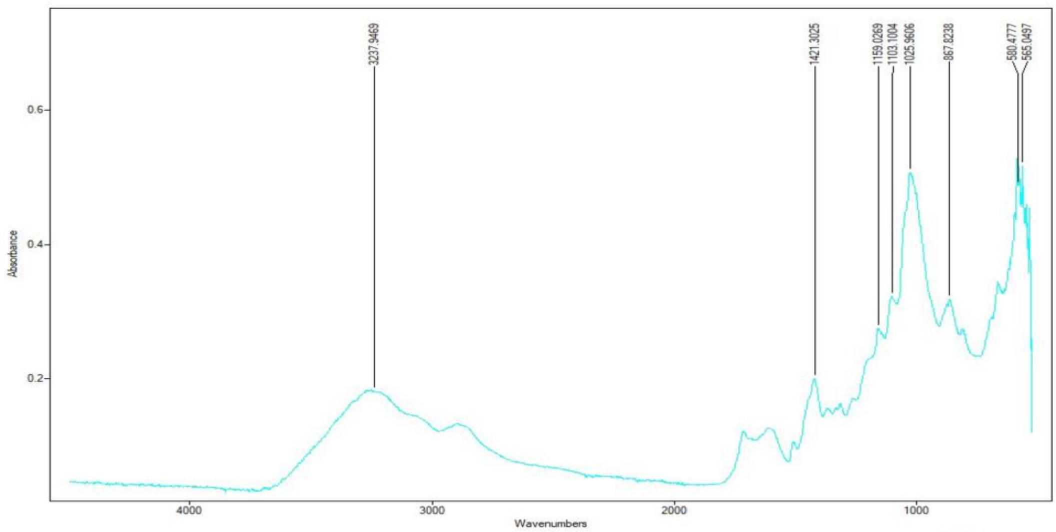
3234.0899 cm-1	1421.3025 cm-1	1159.0289 cm-1	1105.0289 cm-1	1024.0321 cm-1	867.8238 cm-1	576.6207 cm-1	559.2642 cm-1

Figure A.47 — FTIR Image - 0% Ethanol - Dipping method - FTIR spectrum and table of Peak values – Functionalized with PPy



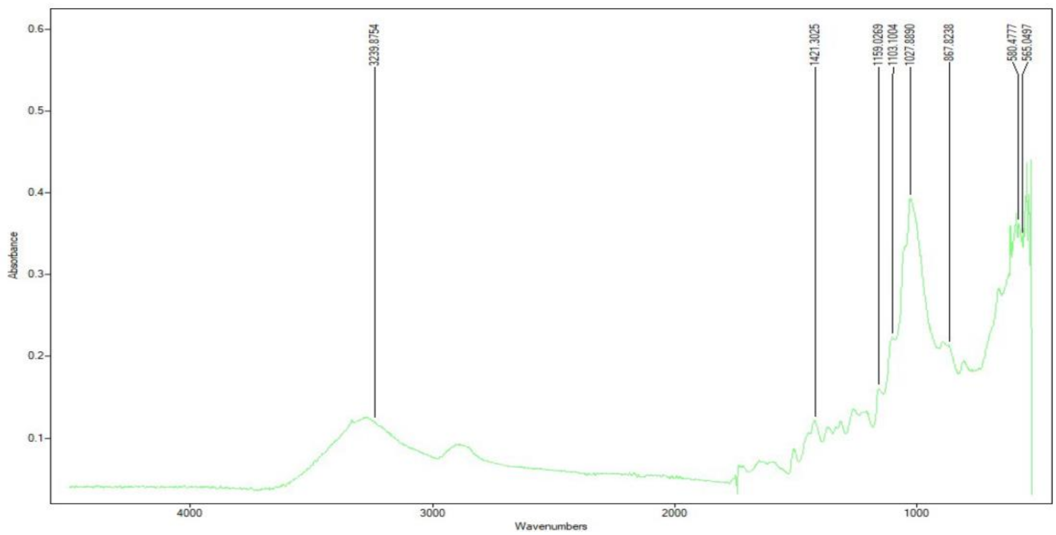
3234.0899 cm-1	1421.3025 cm-1	1159.0269 cm-1	1027.8890 cm-1	867.8238 cm-1	576.8238 cm-1	576.6207 cm-1	559.2642 cm-1

Figure A.48 — FTIR Image - 0% Ethanol - Drop-cast method - FTIR spectrum and table of Peak values – Functionalized with PPy



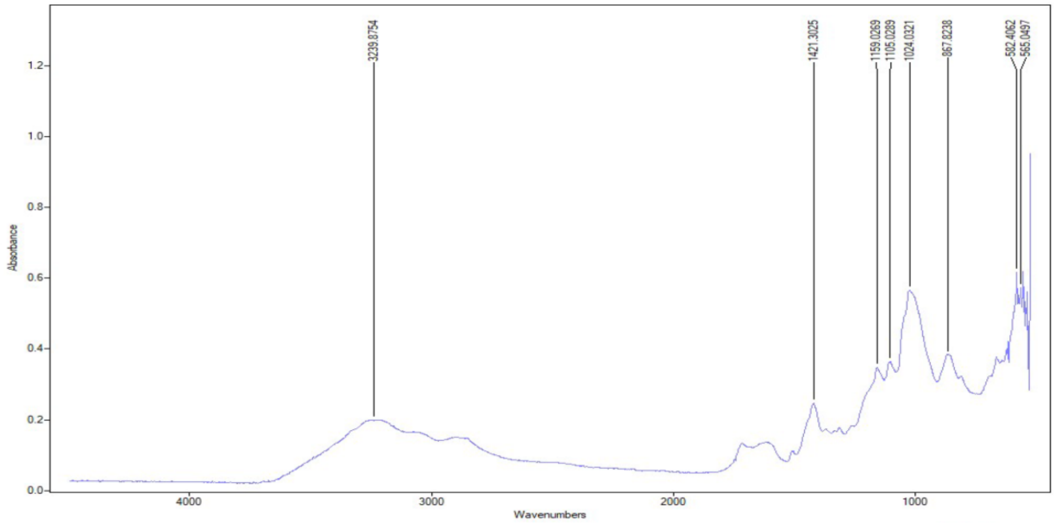
3237.9469 cm-1	1421.3025 cm-1	1159.0269 cm-1	1103.1004 cm-1	1025.9606 cm-1	867.8238 cm-1	580.477 cm-1	565.0497 cm-1

Figure A.49 — FTIR Image - 20% Ethanol - Dipping method - FTIR spectrum and table of Peak values – Functionalized with PPy



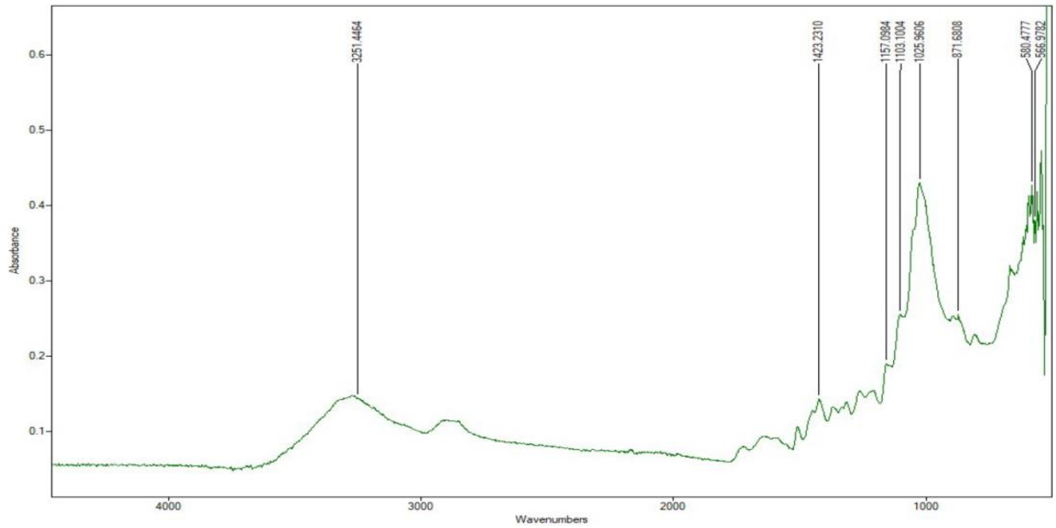
3239.8754 cm-1	1432.3025 cm-1	1159.0269 cm-1	1103.1004 cm-1	1027.8890 cm-1	867.8238 cm-1	580.4777 cm-1	565.0497 cm-1

Figure A.50 — FTIR Image - 20% Ethanol - Drop-cast method - FTIR spectrum and table of Peak values – Functionalized with PPy



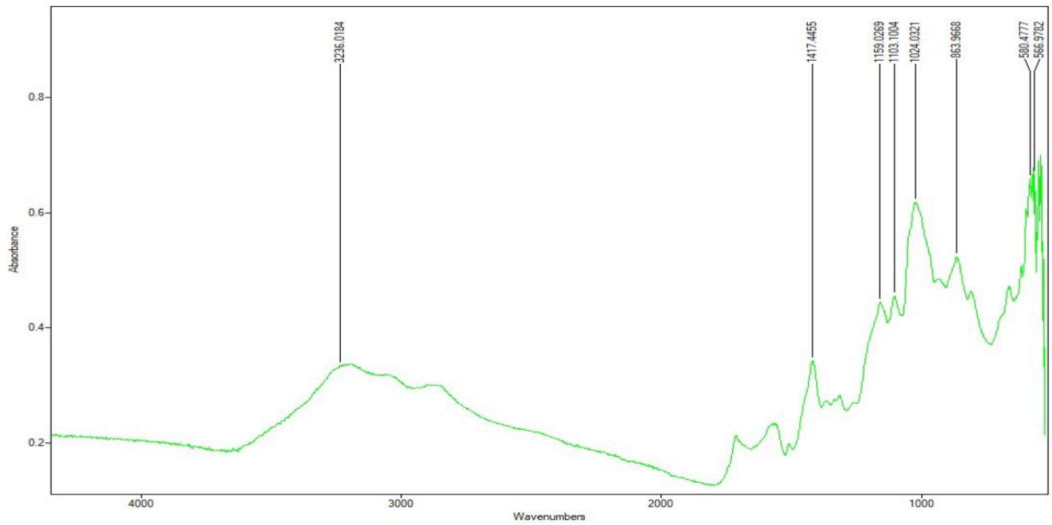
3239.8754 cm-1	1421.3025 cm-1	1159.0269 cm-1	1105.0289 cm-1	1024.0321 cm-1	867.8238 cm-1	582.4062 cm-1	565.0497 cm-1

Figure A.51 — FTIR Image - 50% Ethanol - Dipping method - FTIR spectrum and table of Peak values – Functionalized with PPy



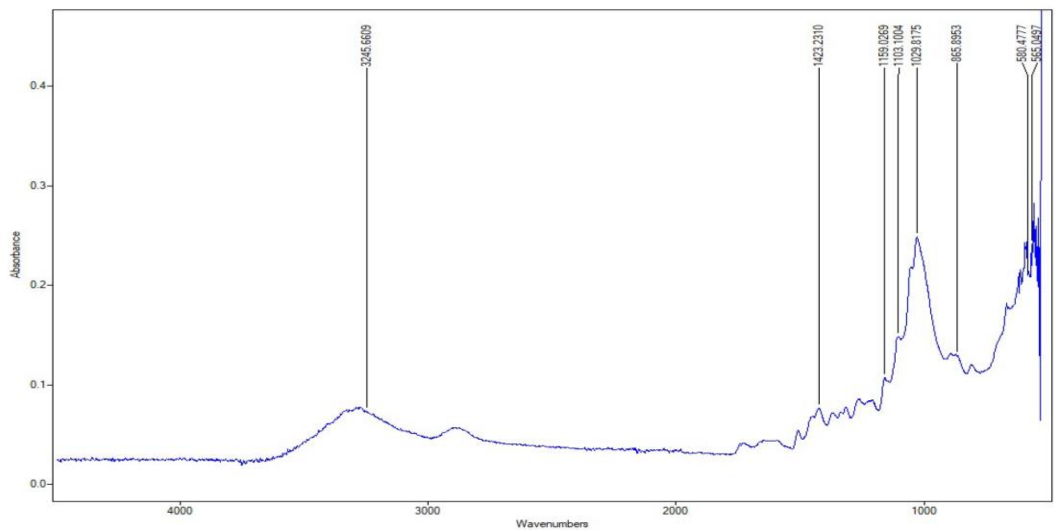
3251.446 cm-1	1423.2310 cm-1	1157.0984 cm-1	1103.1004 cm-1	1025.9606 cm-1	871.6808 cm-1	580.4777 cm-1	566.9782 cm-1

Figure A.52 — FTIR Image - 50% Ethanol - Drop-cast method - FTIR spectrum and table of Peak values – Functionalized with PPy



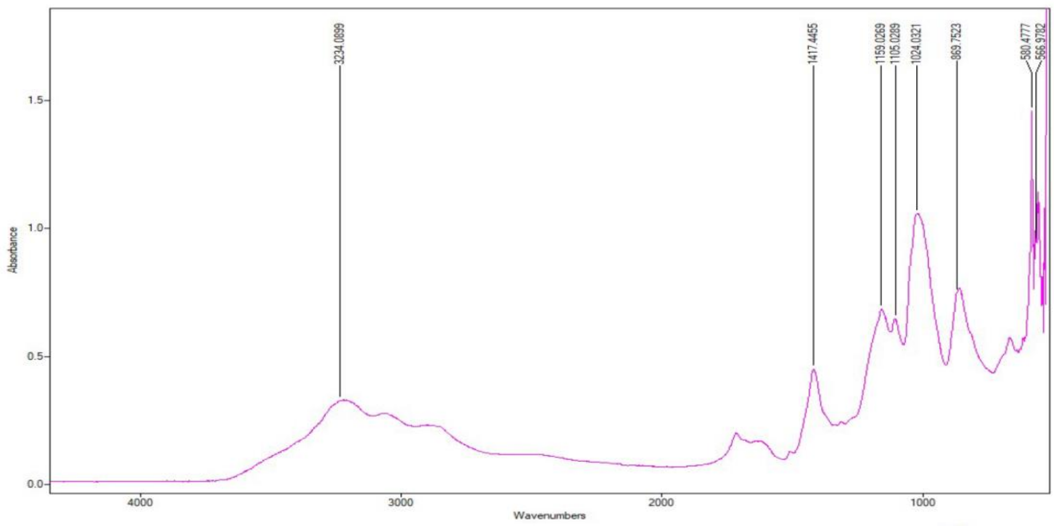
3236.0184 cm-1	1417.4455 cm-1	1159.0269 cm-1	1103.1004 cm-1	1024.0321 cm-1	863.9668 cm-1	580.4777 cm-1	566.9782 cm-1

Figure A.53 — FTIR Image - 80% Ethanol - Dipping method - FTIR spectrum and table of Peak values – Functionalized with PPy



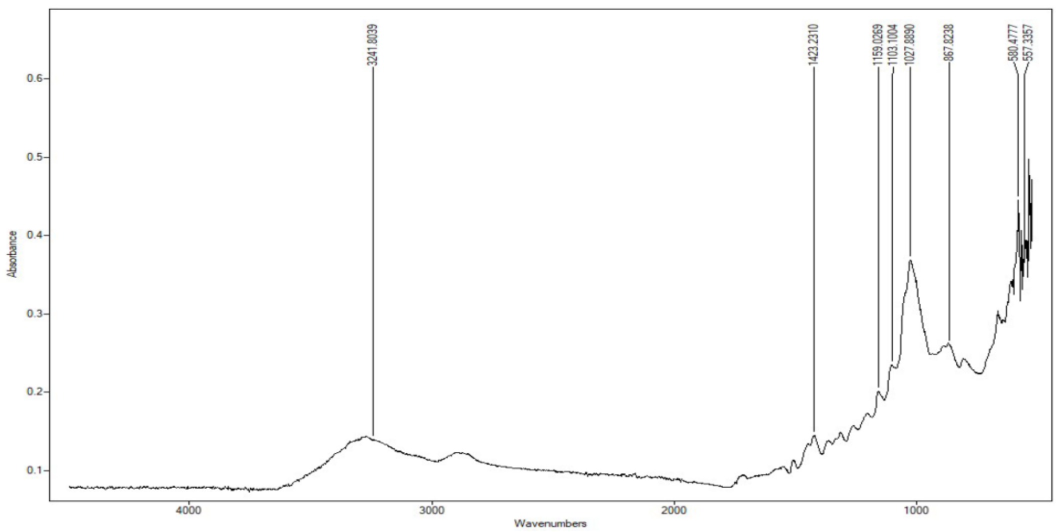
3245.6609 cm-1	1423.2310 cm-1	1159.0263 cm-1	1103.1004 cm-1	1029.8175 cm-1	865.8953 cm-1	580.4777 cm-1	565.0497 cm-1

Figure A.54 — FTIR Image - 80% Ethanol - Drop-cast method - FTIR spectrum and table of Peak values – Functionalized with PPy



3234.0899 cm-1	1417.4455 cm-1	1159.0269 cm-1	1105.0289 cm-1	1024.0321 cm-1	869.7523 cm-1	580.4777 cm-1	566.9782 cm-1

Figure A.55 — FTIR Image - 100% Ethanol - Dipping method - FTIR spectrum and table of Peak values – Functionalized with PPy



3241.8039 cm-1	1423.2310 cm-1	1159.0269 cm-1	1103.1004 cm-1	1027.8890 cm-1	867.8238 cm-1	580.4777 cm-1	557.3357 cm-1

Figure A.56 — FTIR Image - 100% Ethanol - Drop-cast method - FTIR spectrum and table of Peak values – Functionalized with PPy

A.3. Electrical Analysis

From the **Figure A.57 to Figure A.60** are the graphics of 0% Ethanol that was dipped with PPy as an example of the types of graphs that were obtained in order to determine voltage and current.

This is just one recycled paper substrate served as an example. Showing all the graphs of all the recycled paper substrates would take dozens of pages and the procedure to obtain the data is similar to all recycled paper substrates.

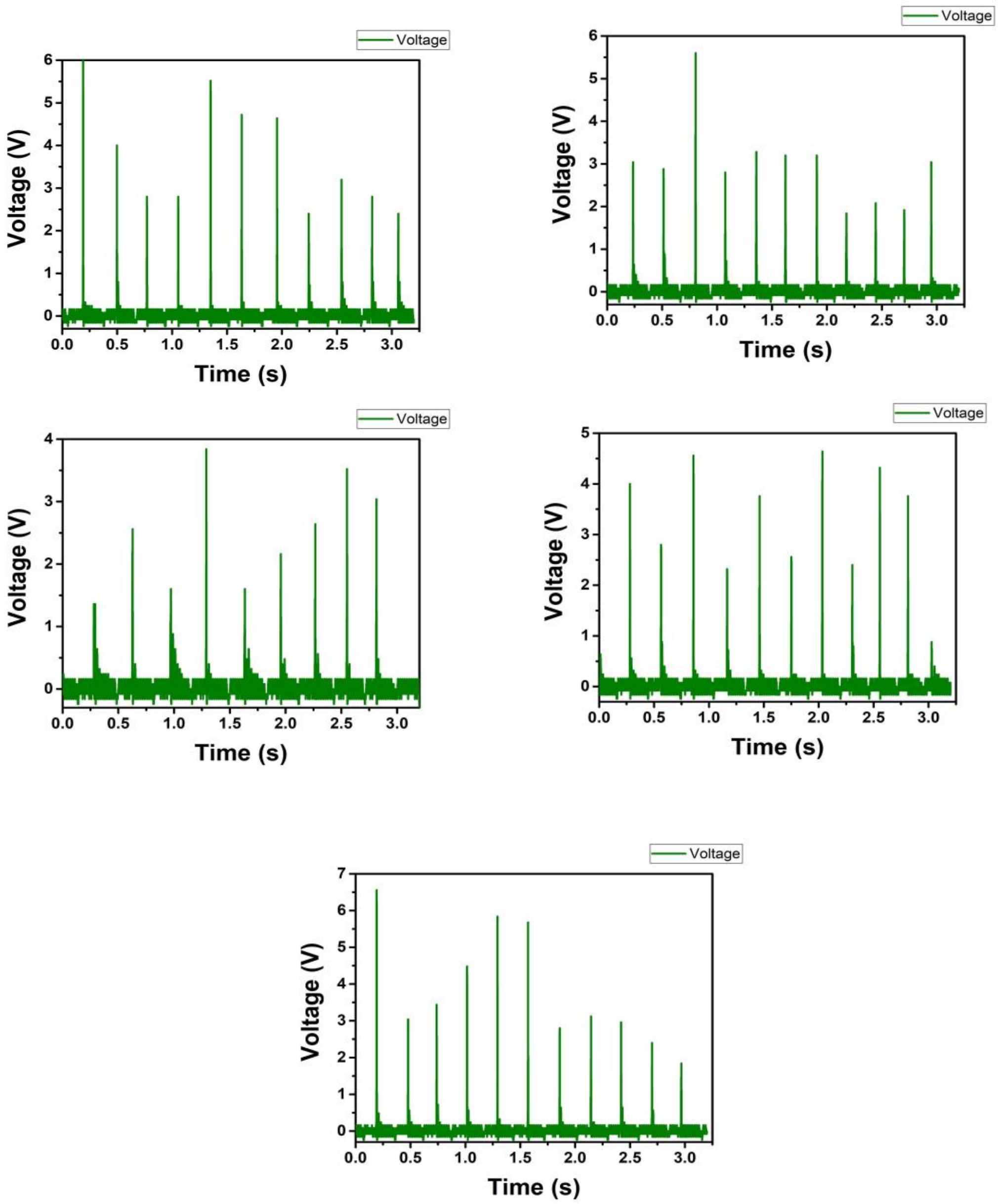


Figure A.57 — Five graphics obtained from oscilloscope that show Voltage (V) and Time (s) – 0% Ethanol - Short Circuit Current

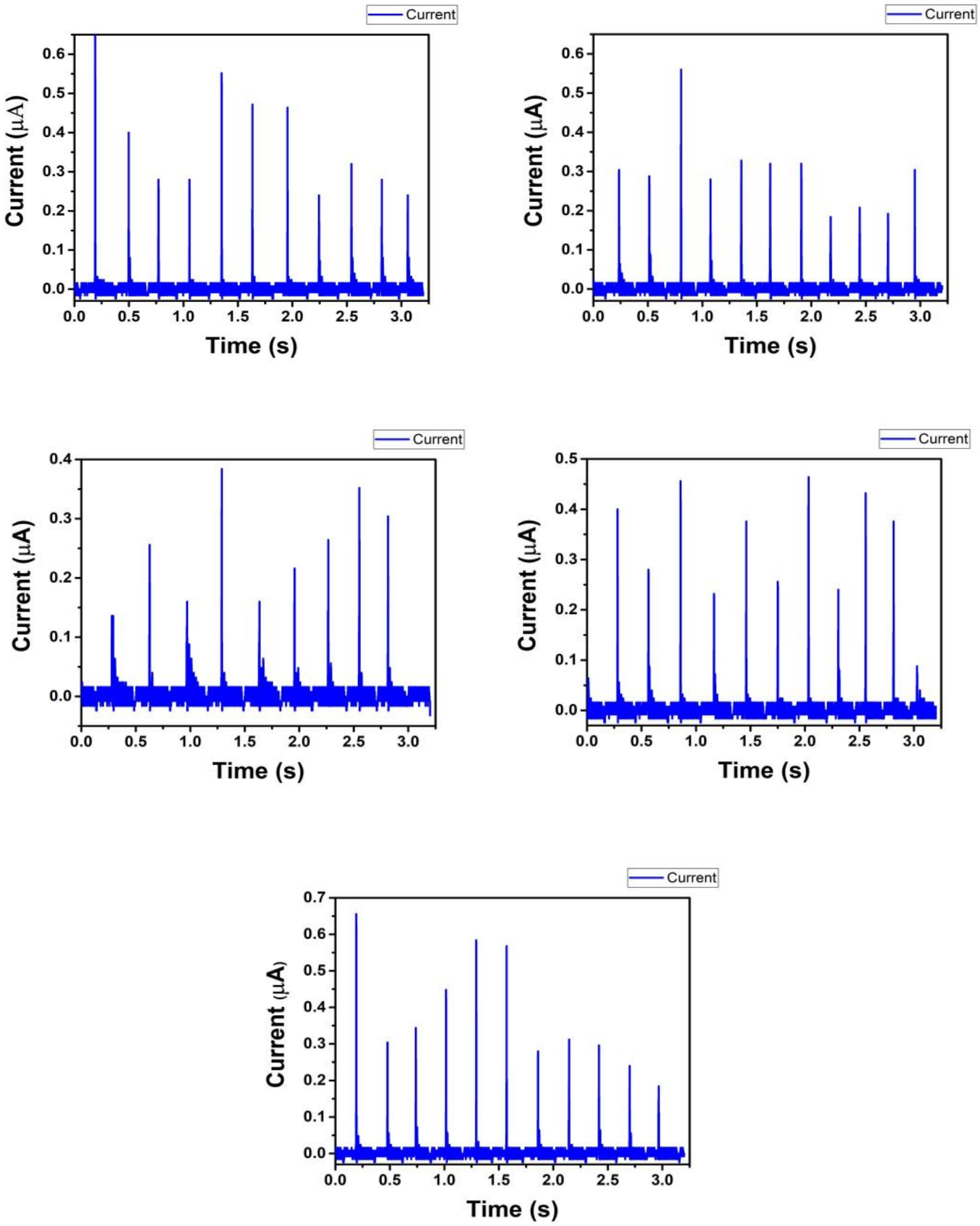


Figure A.58 — Five graphics obtained that show Current (I) and Time (s) – 0% Ethanol – Short Circuit Current

Figure A.57 and Figure A.58 are related to Short Circuit Current. Figure A.59 and Figure A.60 are Open Circuit Voltage graphs. In this instance there were only graphs obtained but the majority of recycled paper substrates it was possible to obtain five.

Figure A.58 was obtained from Figure A.57 and Figure A.60 was obtained from Figure A.59. Both were made converting Voltage to Current using Ohm's Law.

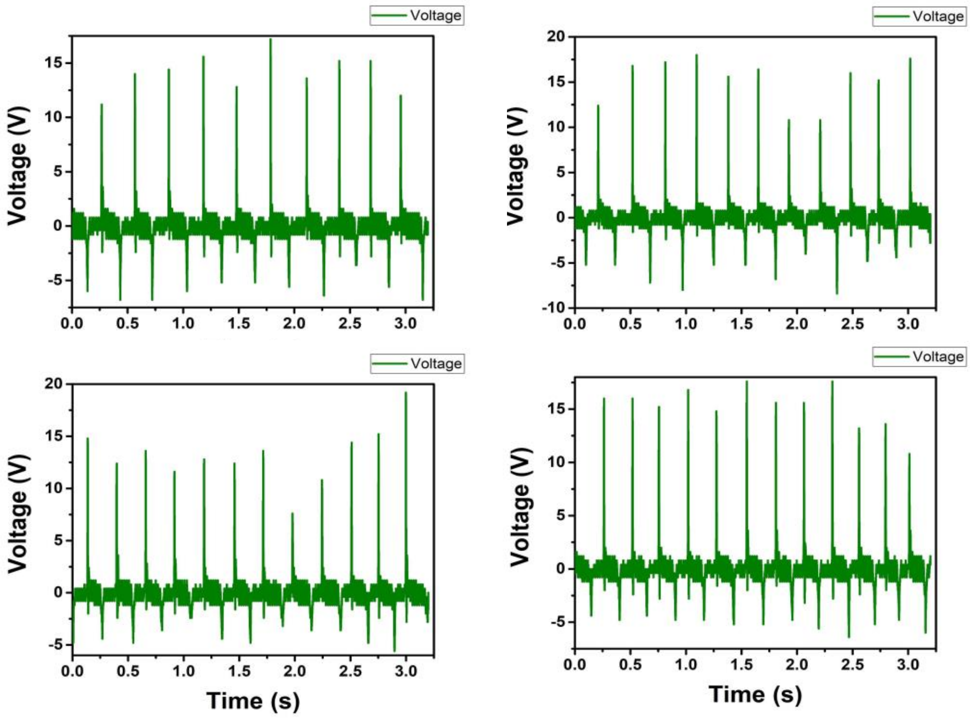


Figure A.59 — Five graphics obtained from oscilloscope that show Voltage (V) and Time (s) – 0% Ethanol - Open circuit Voltage

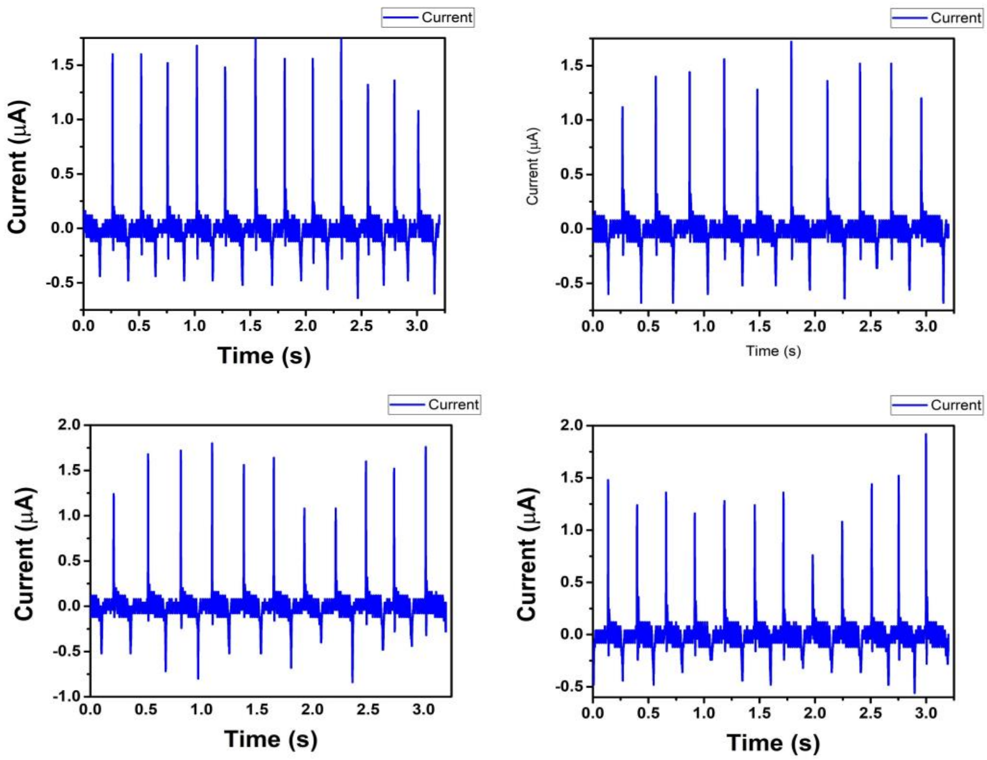


Figure A.60 — Five graphics obtained that show Current (I) and Time (s) — 0% Ethanol - Open circuit Voltage

2022

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Polymeric Functionalization of Recycling Newspaper

NOVA SCHOOL OF SCIENCE & TECHNOLOGY