

# Design of Nanocellulose- mediated hybrid polyaniline electrodes for high performance electronic devices

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Final master thesis

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## **ABSTRACT**

Due to their renewability, extraordinary optical, thermal and mechanical properties, nanostructured cellulose also known as nanocellulose (NCs), namely, cellulose nanofibrils (CNF), cellulose nanocrystals (CNC) and bacterial cellulose (BC) have been used for preparation of nanocomposites. Their usage in electronic devices is quite recent and very promising. In this study, NCs will be produced by chemical routes from natural fibers such as ramie. Isolated NCs will be incorporated into polyaniline (PANI) using different routes to prepare unique porous hybrid PANI/NCs films with desired porosity, pore size distribution and pore interconnectivity.

**Key words:** Polyaniline; Nanocellulose; Polymerization; Characterization; Composite; SEM; thermogravimetric analysis; X-ray diffraction;

## **RESUMEN**

Debido a su renovabilidad, propiedades ópticas, térmicas y mecánicas extraordinarias, la celulosa nanoestructurada también conocida como nanocelulosa (NC), es decir, nanofibrillas de celulosa (CNF), nanocristales de celulosa (CNC) y celulosa bacteriana (BC) se han utilizado para la preparación de nanocompuestos. Su uso en dispositivos electrónicos es bastante reciente y prometedor. En este estudio, las NC se producirán por rutas químicas a partir de fibras naturales como el ramio. Las NC aisladas se incorporarán a la polianilina (PANI) usando diferentes rutas para preparar películas PANI / NC híbridas porosas únicas con la porosidad deseada, la distribución del tamaño de poro y la interconectividad de poros.

**Palabras clave:** Polianilina; Nanocelulosa; Polimerización; Caracterización; Compuesto; SEM; análisis termo gravimétrico; difracción rayos-X

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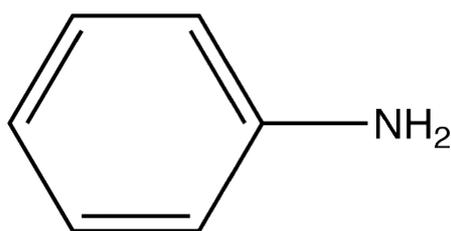
## 1. INTRODUCTION

One of the main problems that technology has to face is energy accumulation and storage so the importance of supercapacitors has increased in the last years. Besides, these supercapacitors can be the best answer to this question due to their high power density and surface area.

Nowadays there are several investigations about supercapacitors made by conductive polymers such as polyaniline which its electrical and conductive properties are good enough to compete with traditional supercapacitors. Conventional supercapacitors are too heavy, thick, rigid, and bulky to fully meet the practical requirements for portable devices due to the presence of inactive components, such as heavy metal substrates, binders, and conductive additives. Besides, there is an urgent need to develop lightweight and flexible ECP-based supercapacitors with high volumetric capacitances [11].

### 1.1 Polyaniline

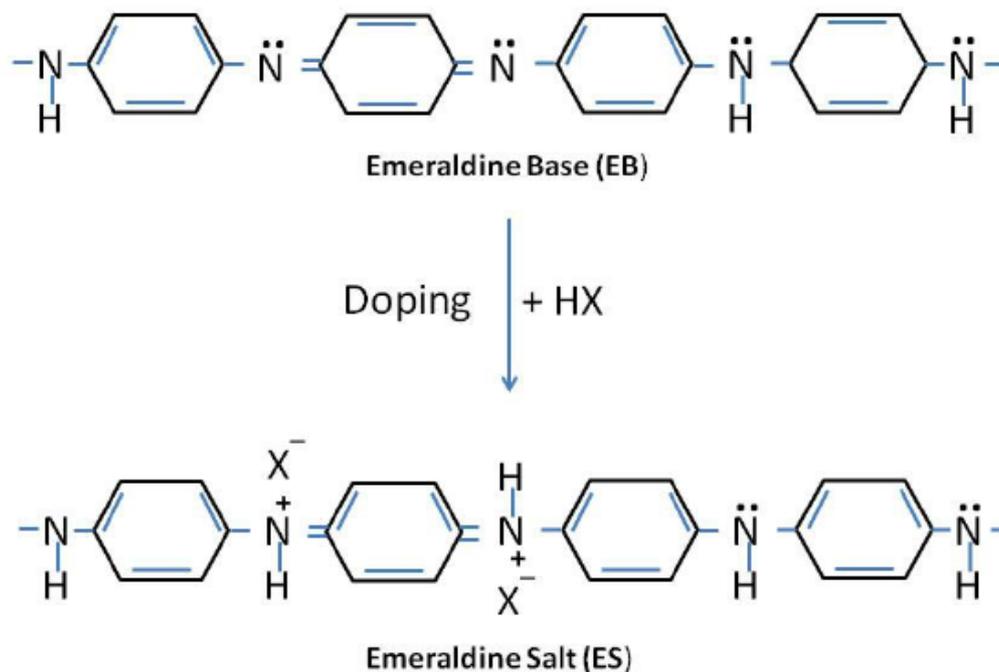
Polyaniline (PANI) is one of the most studied conducting polymers of the past 50 years. Although the compound was discovered over 150 years ago, only since the early 1980s PANI has the current interest due to his high electrical conductivity. PANI belongs to the family of conducting polymers and organic semiconductors and has many attractive processing properties.



*Figure 1: Aniline*

Conductive polymers have unique electrical and thermophysical properties that have enabled their use in a variety of commercial applications. PANI is one of the well-known conducting polymers that has been widely used in numerous applications including supercapacitors, batteries, chemical and biological sensors, electrical conductors. However, PANI has some disadvantages like, for example, low dispersibility and solubility in most solvents and low

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electron transfer rates and conductivity in solutions with a higher pH, which have limited its performance in biosensors and electrical devices.



*Figure 2: PANI Emeraldine form.*

The synergistic effect of the high surface area of the Nanocellulose and the good electronic conductivity of the conducting polymer made the nanocomposite compatible for applications such as in electrochemically controlled ion exchange.

The polymerization of PANI can provide three different oxidation states.

1. Leucoesmeraldine - white/clear and without colour
2. Emerald - green for the emerald salt, blue for the emerald base
3. (per)nigraniline - blue / violet

Studies have shown that most forms of polyaniline correspond to one of the three states or mixtures of these components. The base of emeraldine is considered as the most useful form because of its high speed, temperature and the fact that, on the effect with acid, the emerald salt form of the resulting polyaniline is highly conductive of electricity. The leucoesmeraldine and pernigraniline are poor drivers, even when they are doped with an acid, so it is important to avoid the formation of these two components.

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The colour change associated with polyaniline in different oxidation states can be used in sensors and electrochromic devices. Although colour is useful, the best method for manufacturing a polyaniline sensor is one that takes advantage of the changes produced in the electrical conductivity between the different oxidation states, or doping levels.

This chemical structure is basic for the excellent electrical conductivity of PANI. The importance of getting this structure is crucial to have a competitive conductive polymer. To achieve this emeraldine salt a dopant is needed to improve its conductivity.

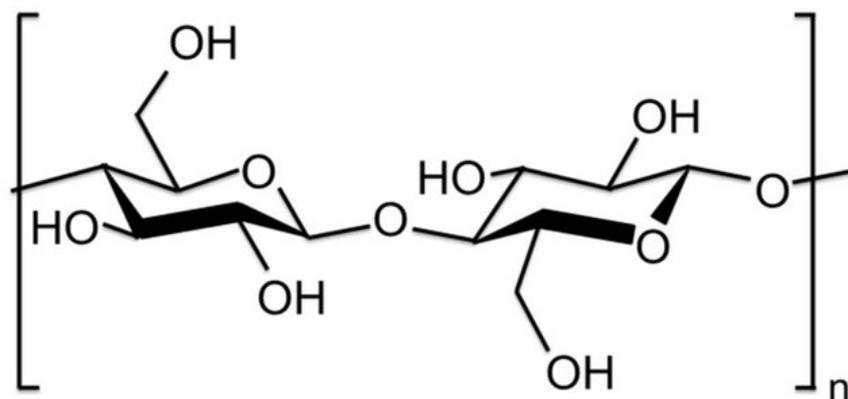
## 1.2 Nanocellulose

Cellulose is nowadays one of the most abundant materials in the world due to its part of plants structure basically. Also, cellulose has a good physical and chemical properties that makes this material interesting for nanomaterials and nanocomposites. The main sources of cellulose are plants, wood, cotton and cellulose bacteria but it also be obtained from agricultural residues with a low cost which makes this material environmental friendly. In this experiment, our source will be natural cotton. [2]

The main physical properties are low density, flexibility, durability and the capacity for make films and aerogels which is useful for combine this material with others. In this case, Nanocellulose Crystals (CNC) and Nanocellulose fibers (CNF) can be obtained from natural cellulose. CNC are crystals with diameter in the range of 3 - 20 nm and length in the range of 100-600 nm. Besides CNC has better properties such as high surface area, mechanical and optical properties and better affinity to create nanocomposites. These properties make CNC the perfect material for applications such as hydrogels, films, optical devices and pharmaceuticals.

One of the most specific characteristics of cellulose is that each of its monomers bears three hydroxyl groups. The ability of these hydroxyl groups to form hydrogen bonds plays a major role in the formation of fibrillar and semicrystalline packing which governs the important physical properties of these highly cohesive materials. [10]

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*Figure 3: Chemical structure of Cellulose.*

One of the disadvantages associated to the utilization of cellulose nanoparticles for preparation of polymer nanocomposites as a reinforcement material is their difficulty to disperse in most of polymeric matrices and particularly in hydrophobic matrices, or in non-polar solvents due to polar nature of their surface, thus leading to the aggregation of nanofillers [2]. Sonication is always needed to disperse CNC in water for the creation of composites. Hydroxyl groups that cover the surface of cellulose allow it to react well with a variety of materials including conducting polymers.

### 1.3 Characterization

For the characterization of the obtained products different techniques will be used. These techniques are the following.

- Scanning Electron Microscopy (SEM)

Scanning electron microscope (SEM) was used to observe the morphology of the nanocomposites at the micro-level. The samples were coated by the 5 nm thin layer of gold and measured by electron microscope Mira 3 LMH (Tescan Brno, s.r.o.; Czech Republic) equipped with Shottky cathode.

#### Fourier Transform Infrared Spectroscopy (FTIR)

The chemical structure of the prepared materials was characterized by Fourier transform infrared (FTIR) spectroscopy in transmission mode. For this purpose, pellets containing the material to be analyzed were prepared using KBr. FTIR spectrometer using a Thermo Scientific Nicolet iZ10-FTIR spectrometer, working with OMNIC Software was utilized. The global was

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*Nanocellulose-mediated hybrid polyaniline electrodes for high performance electronic devices* used as source of mid infrared radiation, KBr was used as beam splitter and DTGS as detector, 128 scans were collected for each spectrum with resolution  $4\text{ cm}^{-1}$ .

- X-Ray Diffractometry (XRD)

The crystalline structure of the prepared materials was determined using X-ray diffraction. The materials were characterized by same methodology. X-ray powder data were measured at room temperature on a  $\theta$ - $\theta$  powder diffractometer X'Pert3Powder in Bragg-Brentano parafocusing geometry using wavelength  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5418\text{ \AA}$ ,  $U = 40\text{ kV}$ ,  $I = 30\text{ mA}$ ). Data were scanned using an ultrafast detector 1D PIXcel angular range  $5\text{-}50^\circ$  ( $2\theta$ ) with a step size of  $0.039^\circ$  ( $2\theta$ ) and a counting time of 175.185 s per step. Data evaluation was done by HighScorePlus 4.0.

- Conductance measurements

Specific conductance measurements were carried out using an apparatus constructed according to Medek. Values of specific conductance were evaluated from Ohm's law and known geometrical dimensions.

- Thermogravimetric Analysis (TGA)

The thermal stability and degradation behaviour of the synthesised materials were investigated by Thermogravimetric Analysis (TGA). TGA measures how the mass of the materials change as a function of increasing temperature under an air atmosphere. The mechanisms of degradation give insight in to the chemical composition of the materials. TGA measurements were carried out using Stanton-Redcroft TG 750 in nitrogen ( $20\text{ ml min}^{-1}$ ) at a heating rate of  $10^\circ\text{C/min}$  from room temperature to  $800^\circ\text{C}$

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## 2. EXPERIMENTAL

### 2.1 Obtaining Nanocellulose Crystals

CNC can be obtained from a lot of different sources so in this case the source is going to be natural cotton. This raw cotton has impurities which must be removed before starting the hydrolysis. For this reason, the first step is bleaching the fibres.

#### 2.1.1 Bleaching

Bleaching was necessary to remove organic residues such as lignin and hemicelluloses while leaving cellulose moieties intact if optimal conditions are respected. Therefore, 1 liter sodium hydroxide solution of 4 wt% was prepared and stirred for 10 minutes to obtain a homogenous solution. The fibers were cut into smaller pieces in range of millimeters.

Multiple batches of 15 grams were prepared as two times 7.5 grams. This was done because increasing the amount of fibers increases the viscosity and hence makes the stirring more difficult. A ratio of 1 liter NaOH per 15 grams of fibre was used. Resulting in adding 500 ml per Erlenmeyer. The 7.5 grams of fibres were added per Erlenmeyer, with a total of 2 Erlenmeyer's.

For the first step the dispersion was stirred at 500 rpm for 2 hours at a temperature of 80 °C. After this, the solution was filtered in a glass Büchner filter. No filter paper was used because of clogging.

The fibres were washed using about 400 ml deionized water at a time, for both filters. The solution was again stirred and filtered. This process was repeated until the permeate pH was almost neutral. The pH was checked using universal pH paper. The primary washing was done 10 times to achieve neutral pH.

The second step was to dilute the washed ramie fibres in 500 ml of NaOH solution per 7.5 gram of fiber. The same concentration of solution was used. The fibers were washed as in step 1 and the primary washing was done 15 times.

After washing the fibres were dried in a drying oven at 50 °C under a pressure of 200 mbar for 5 days. Every hour the drying was interrupted to detach the fibres so smaller particles were obtained which would be both faster to dry and necessary for the next step.

$$\frac{4 \text{ g NaOH}}{96 \text{ g H}_2\text{O}} = \frac{4 \text{ g NaOH}}{0.096 \text{ L H}_2\text{O}} \Rightarrow 1 \text{ L} \equiv 41.67 \text{ g NaOH}$$

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$$\text{Calculated concentration: } \frac{41.67 \frac{\text{g}}{\text{L}}}{40.0 \text{ g/mol}} = 1.04 \text{ M}$$

### 2.1.2 Hydrolysis

Cellulose fibers do not display a regular surface. This means that next to the crystalline phase they also appear in an amorphous phase. This increase the rigidity and the formation of extensive intra and intermolecular hydrogen bonding that causes insolubility in water. These amorphous regions are susceptible to acid attacks. So, the acid hydrolysis induces a rapid decrease in its degree of polymerization (DP), which is called the level-off DP. The most commonly used acids are sulfuric acid and hypochlorite acid, but only the former creates a stable suspension in water when it comes to the treatment of ramie fibres.

After hydrolysis, the nanoparticles will have a crystalline structure like the original cellulose fibres. It is possible to have a yield up to 30%. The other part consists out of microfibers and an unreacted amorphous phase.

First, 64 V% sulfuric acid solution was prepared. This was done in a 250 ml volumetric flask. The solution was stirred and deionized water was added until a 250 ml homogenous solution was achieved. The solution was left resting until it was at room temperature, which took 3 hours to achieve. A ratio of 12 ml acid per gram of fibers was used and the hydrolysis was performed under reflux.

For the hydrolysis of 5 grams 60 ml of acid was added to a 250 ml three-neck round flask. The fibers were added first and then the stirring system and the thermometer. The acid was added first the 60 ml and after that, more acid was added to be able to measure the temperature.

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*Figure 4: Hydrolysis of CNC*

The flask was put under reflux and stirred at 630 rpm and heated until the solution reached a temperature of 50 °C. When the temperature increase is too fast or when the temperature of the solution goes above the 55 °C the fibres start to burn. This can be seen by a yellow/brownish colour and should be avoided at all costs.

After 45 minutes of acid hydrolysis at a temperature of 50 °C the reaction was stopped by pouring cold water into the round flask. The solution was then washed using the centrifuge for 12 minutes at 14500 rpm. The supernatant was replaced with deionised water. The tubes were shaken and put into the centrifuge. The washing was done for 4 times, after this we can see losses in the supernatant so is the moment to stop centrifuging and continue the next step.

Before continuing the washing the ultra-turax was applied for 1 minutes at 9000 rpm to resuspend the particles. Hereafter, the solution containing the cellulose nanoparticles was

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Figure 5: CNC after dialysis ready for freeze-drying.

Sonication was applied as a form of energy to break the aggregates into smaller particles. The solution was sonicated for 3 minutes at 40 W. To get rid of the aggregates that are still present in the solution and possible dust particles the solution was filtered under vacuum before being stored in the freezer.

Besides, freeze-drying was used to dry the CNC and after that it was storage in a bottle ready for the reaction with PANI.

$$w_1 = 96 \% ; \rho_1 = 1.83 \frac{g}{ml} \text{ (at } 20 \text{ }^\circ\text{C)} ;$$

$$w_2 = 64 \% ; \rho_1 = 1.542 \frac{g}{ml} \text{ (at } 20 \text{ }^\circ\text{C)} ; V_2 = 250 \text{ ml}$$

$$w_1 \times m_1 = w_2 \times m_2$$

$$\rho = \frac{m}{V} \Leftrightarrow m = \rho * V$$

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$$V_1 = \frac{w_2}{w_1} \times \frac{\rho_2}{\rho_1} \times V_2$$

$$V_1 = \frac{0.64 \cdot 1.542}{0.96 \cdot 1.83} \cdot 250 = 141 \text{ ml of } H_2SO_4$$

## 2.2 Obtaining Polyaniline

Some experiments were done to make sure which amount of solid content is the correct one to run the experiments with both components.

### 2.2.1 PANI 3%

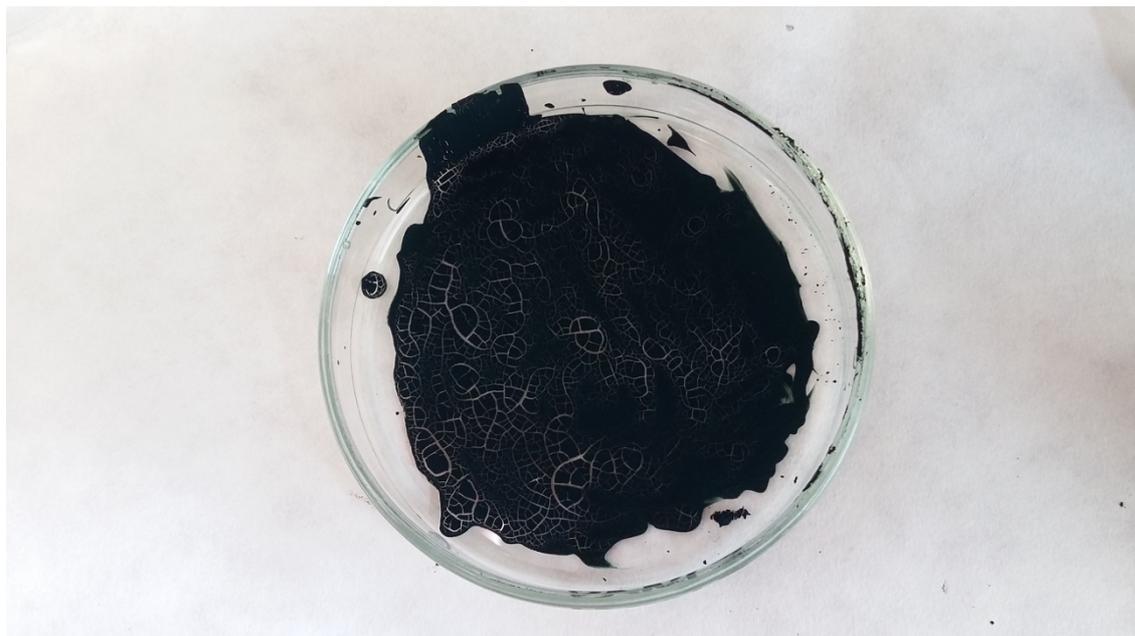
The solid content for this PANI experiment was 3% and the ratio of initiator used was 1'25 APS/PANI. The volume was set at 20 mL so the calculations are the following:

$$20g \cdot 0,03 = 0,6g \text{ ANI } V_{ANI} = \frac{0,6}{1,022} = 0,587 \text{ mL}$$

$$0,6g \cdot 1,25 = 0,75g \text{ APS}$$

2 mL of 1M HCl solution was saved for dilute APS and the rest was directly on the beaker. The reaction was performed all the time in ice bath. Two experiments were done, one under stirring conditions and other under stagnant conditions. After 24h the solution was washed with 0,2M HCl in a filter paper and the solid content was collected. Half of the sample was saved at room temperature and the other half was freeze-drying.

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*Figure 6. Stagnant conditions at room temperature.*

### 2.2.2 PANI 5%

Same procedure was followed for the experiment with 5% solid content. The calculations were the next:

$$20g * 0,05 = 1g \text{ ANI } V_{\text{ANI}} = \frac{1}{1,022} = 0,978 \text{ mL}$$

$$1g * 1,25 = 1,25g \text{ APS}$$

So, 2,5 mL was saved to dilute APS in a 5-mL beaker and the samples were saved at room temperature and freeze-drying.

### 2.2.3 PANI 8%

Same procedure was followed for the experiment with 8% solid content. The calculations were the following:

$$20g * 0,08 = 1,6g \text{ ANI } V_{\text{ANI}} = \frac{1,6}{1,022} = 1,566 \text{ mL}$$

$$1,6g * 1,25 = 2g \text{ APS}$$

So, 3 mL was saved to dilute APS in a 5-mL beaker and the samples were saved at room temperature and freeze-drying.

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*Figure 7: PANI 8% freeze-drying*

#### 2.2.4 PANI 8% Not Washed

Other experiment with PANI and 8% solid content was performed for comparing the results with and without the washing step. For this experiment the only change was not making the washing step and saving the samples at room temperature and freeze-drying when the reaction is done. The calculations are the same than the PANI 8% experiment. The sample at room temperature showed a lot of side products that contaminated the main product so only the freeze-dried sample was analyzed.

## 2.3 Obtaining Polyaniline-Nanocellulose composites

### 2.3.1 PANI-CNC 10%-10%

First, an experiment with 10% of solid content was made to see if it is possible to create the film in one shot. The reaction at 10% solid content is very fast and it last only few seconds to finish.

For this experiment, we are going to set a volume, which will be 10mL and a 10% wt of PANI-CNC. The solid content will be 90% ANI and 10% CNC and all the solids will be dispersed in 1M HCl solution. The amount of APS used as initiator will be 1'25 APS/ANI.

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The previous calculations are the following:

$$10g * 0,1 = 1g$$

$$1g * 0,9 = 0,9g \text{ ANI} \rightarrow V_{ANI} = \frac{0,9}{1,022} = 0,881 \text{ mL}$$

$$1g * 0,1 = 0,1g \text{ CNC}$$

$$0,9 * 1,25 = 1,125g \text{ APS}$$

So, we are going to use 1mL for having ANI in acidic conditions and 1.5 mL for dissolve APS, so the final volume to disperse the CNC would be:

$$10 - 1 - 1,5 - 0,881 = 6,619 \text{ mL}$$

First step is to pipette ANI in a 50mL-beaker and 1 mL of HCl solution under stirring condition and cover it with Parafilm. Next step is to prepare the APS that was weighed in a 5mL-beaker and diluted in HCl solution under stirring conditions.

After that, CNC was weighed and dispersed in HCl solution and sonicate for 1 hour. Meanwhile, ice bath was prepared for ANI to have the solution at correct temperature for polymerization and the petri dish has to be ready for casting.

When the sonication is finished, CNC is dropped to the ANI solution and then the APS. The reaction is very fast so few seconds after the solution was casted in the petri dish to form a film. The film was let to dry overnight.

The result of the Petri dish was the following:



*Figure 8: PANI-CNC 10%*

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The main problem that was found was the aggregation of CNC and the phase separation that occurred between PANI and CNC. It is possible to observe in the figure 7 small white points related to the CNC. Due to this separation, the result was not a film just powder.

#### 2.3.2 PANI-CNC 5%-10%

We are going to decrease the solid content to 5% because the reaction will be slower and the aggregation of PANI-CNC will be better. So, for this experiment, the calculations are:

$$20g * 0,05 = 1g$$

$$1g * 0,9 = 0,9g \text{ ANI} \rightarrow V_{ANI} = \frac{0,9}{1,022} = 0,881 \text{ mL}$$

$$1g * 0,1 = 0,1g \text{ CNC}$$

$$0,9 * 1,25 = 1,125g \text{ APS}$$

Now, we are going to mix the ANI with CNC and sonicate them together, so this way there is no need to save 1 mL for having ANI in acidic conditions. The volume of HCl that we have now to disperse CNC and ANI is:

$$20 - 3,34 - 0,881 = 15,77 \text{ mL}$$

The reaction was performed all the time in ice bath. After 24h the solution was washed with 0,2M HCl in a filter paper and the solid content was collected. Half of the sample was kept at room temperature and the other half was freeze-drying.

#### 2.3.3 PANI-CNC 8%-10%

A new batch of PANI-CNC is going to be made for 8% solid content and the same procedure was followed as the experiment above. The calculations now are:

$$20g * 0,08 = 1,6g$$

$$1,6g * 0,9 = 1,44g \text{ ANI} \rightarrow V_{ANI} = \frac{1,44}{1,022} = 1,409 \text{ mL}$$

$$1,6g * 0,1 = 0,16g \text{ CNC}$$

$$1,44 * 1,25 = 1,8g \text{ APS}$$

So, we are going to use 1mL for having ANI in acidic conditions and 4,5 mL for dissolve APS, so the final volume to disperse CNC would be:

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$$20 - 4,5 - 1,409 = 14,091 \text{ mL}$$

The reaction was performed all the time in ice bath. After 24h the solution was washed with 0,2M HCl in a filter paper and the solid content was collected. Half of the sample was keep at room temperature and the other half was freeze-drying.

*2.3.4 PANI-CNC 8%-20%*

Same experiment is going to be made but now we are going to increase the solid content of CNC to 20%. The calculations are:

$$20g * 0,08 = 1,6 \text{ g}$$

$$1,6g * 0,8 = 1,28g \text{ ANI} \rightarrow V_{ANI} = \frac{1,28}{1,022} = 1,252 \text{ mL}$$

$$1,6 \text{ g} * 0,2 = 0,32 \text{ g CNC}$$

$$1,28 * 1,25 = 1,6g \text{ APS}$$

So, we are going to use 1mL for having ANI in acidic conditions and 2,5 mL for dissolve APS

$$20 - 2,5 - 1,252 = 16,248 \text{ mL}$$



*Figure 9: PANI 8% 20% at room temperature*

The reaction was performed all the time in ice bath. Two experiment were done, one under stirring conditions and other under stagnant conditions. After 24h the solution was washed with

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0,2M HCl in a filter paper and the solid content was collected. Half of the sample was kept at room temperature and the other half was freeze-drying.

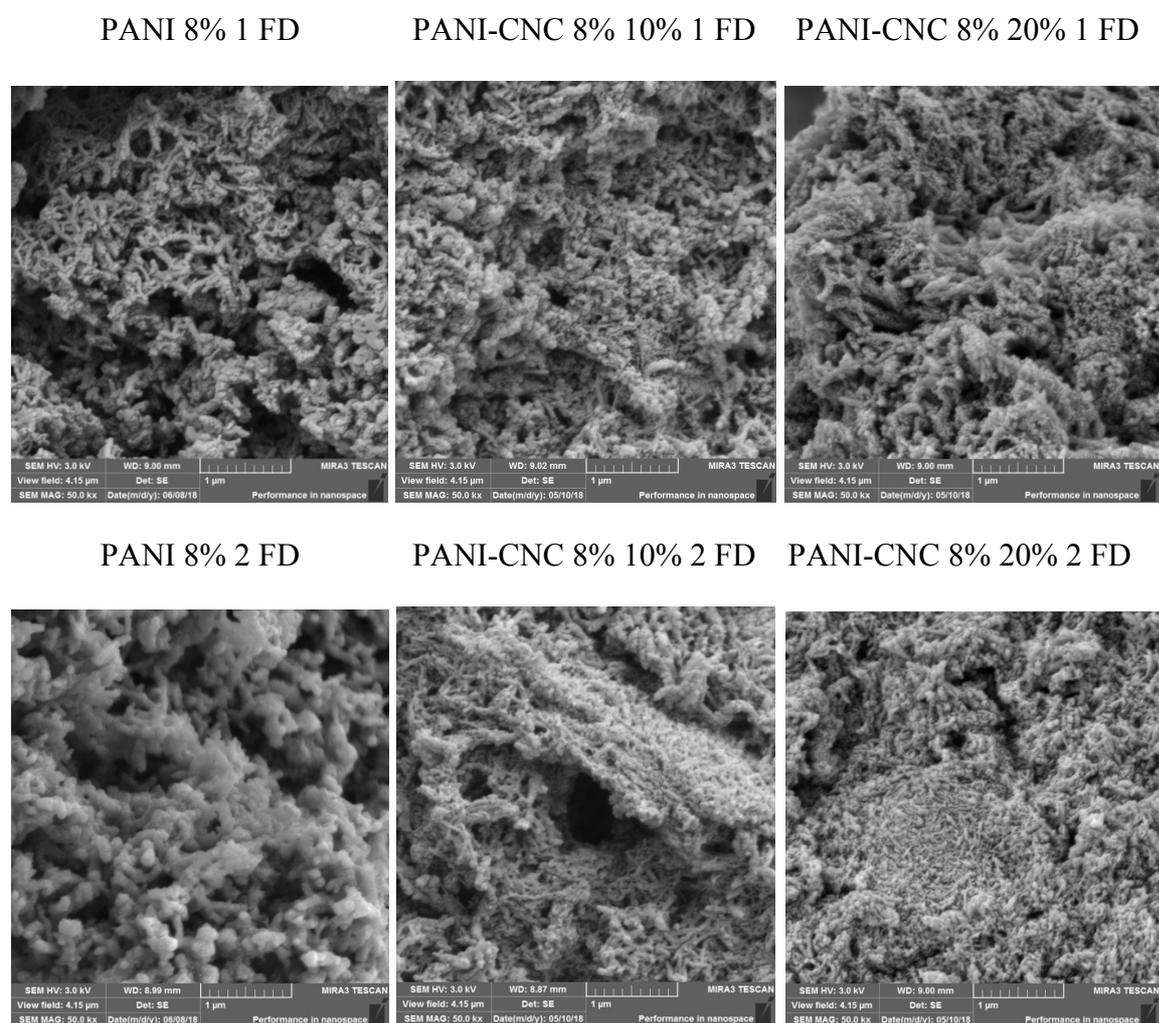
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### 3. RESULTS

For making easier the way of naming the samples, the samples have been named by the material (PANI or PANI-CNC), the percentage of solid content (first number of the sample), the solid content of CNC (second number of the sample), stirring or stagnant conditions (1 or 2 respectively) and the way of drying the sample, room temperature or freeze-drying (RT or FD).

#### 3.1 Morphology

SEM images were used for the characterization of the morphology of the composites.



*Figure 10: SEM images*

On figure, we can see that the morphology of the composites do not change but some differences can be appreciated. First of all, we can confirm that PANI is added to the surface of CNC, creating more compact composite due to the aggregation of CNC with PANI. Also, the

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 samples that reacted at stagnant conditions show less porous than the samples that reacted at stirring conditions. All the PANI samples show an irregular morphology so we can say that the morphology of the samples are mostly amorphous [5].



*Figure 11: PANI 8% not washed*

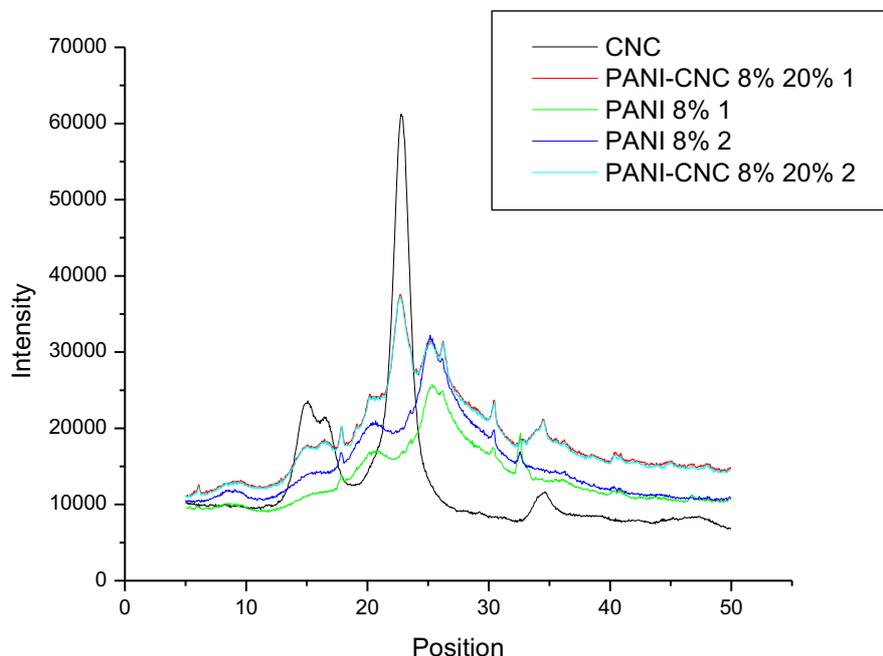
In this sample, we can see a crystallinity morphology of the PANI that was not washed. But this crystallinity is associated to the reaction impurities that was not removed from the PANI. For this reason, even if we lose some crystallinity, the washing step is mandatory for having a composite without impurities.

### 3.2 Chemical structure

For knowing the chemical structure of the composite the samples were characterized by X-Ray Diffraction and FT-IR.

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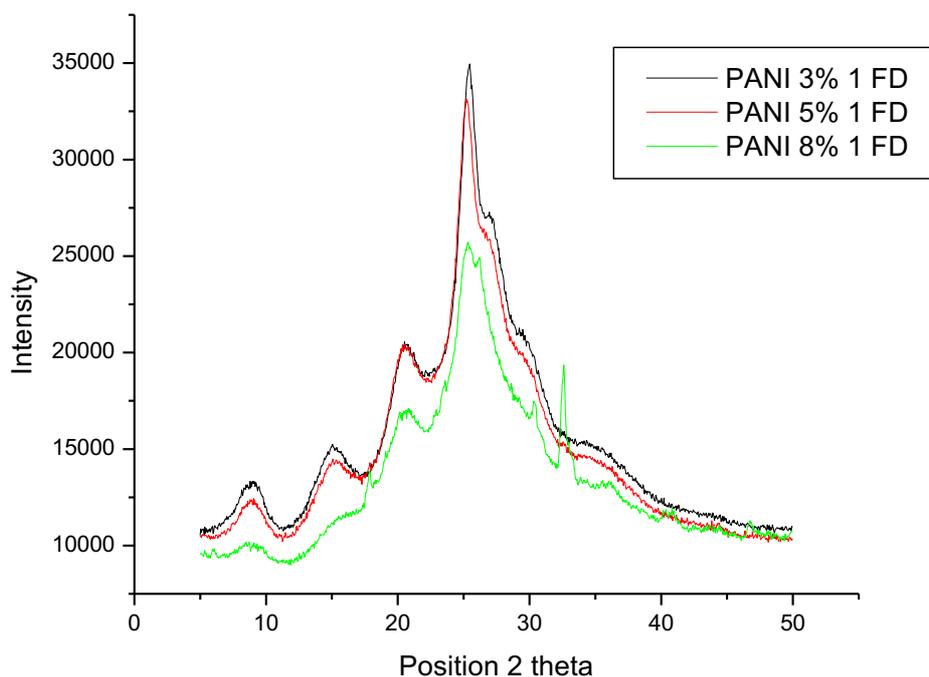
3.2.1 *X-Ray diffraction analysis*



*Figure 12: Comparison PANI 8% FD and PANI-CNC 8% 20% FD*

Here we can observe that there are no differences between stirring and stagnant conditions because the graphics are very similar. The peaks that pure PANI presents are mainly at  $2\theta=20^\circ$  and  $2\theta=25^\circ$  corresponding to (020) and (200) crystal planes [7]. These positions are related to form of emeraldine salt and the presence of quinonoid and benzenoid rings so this proves that our PANI has the composition that we want. The highest peak at  $2\theta=25^\circ$  reveal that the semi-crystalline structure of our material but at the same time shows an amorphous percentage.

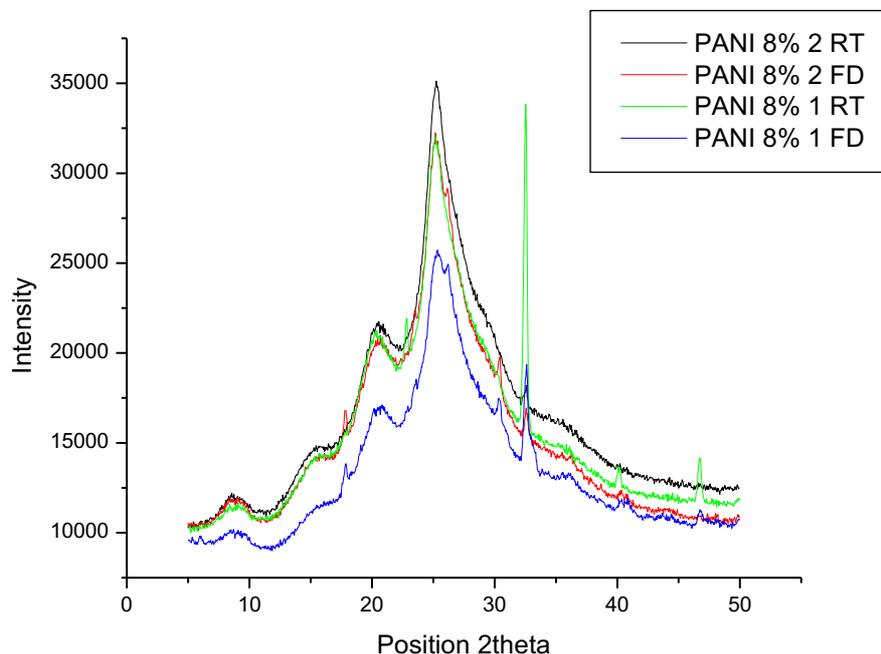
We can also see the peaks of PANI-CNC that are the same that PANI and CNC separated. The peaks corresponding to the characteristics peaks of both materials are in the PANI-CNC graphics. Due to this, we can assume that PANI has been added to the surface of crystalline cellulose. We can also say that the crystallinity of the composite is higher than PANI but less than CNC. To increase the crystallinity of the composite the percentage of CNC should be higher.

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*Figure 13: Comparison PANI 3%, 5% and 8%*

In this graphic we can see a comparison of PANI with different solid content that we used for the preparation of the samples. As the graphic shows, there is no difference between the main peaks and the intensity of them and only PANI 8% has a different peak. According to the report from the central lab, this peak is related to Hydrogen Ammonium Sulfate which it means that some initiator has reacted with the dopant and formed a complex. This prove that the washing step is necessary to remove all this impurities that can appear during the reaction.

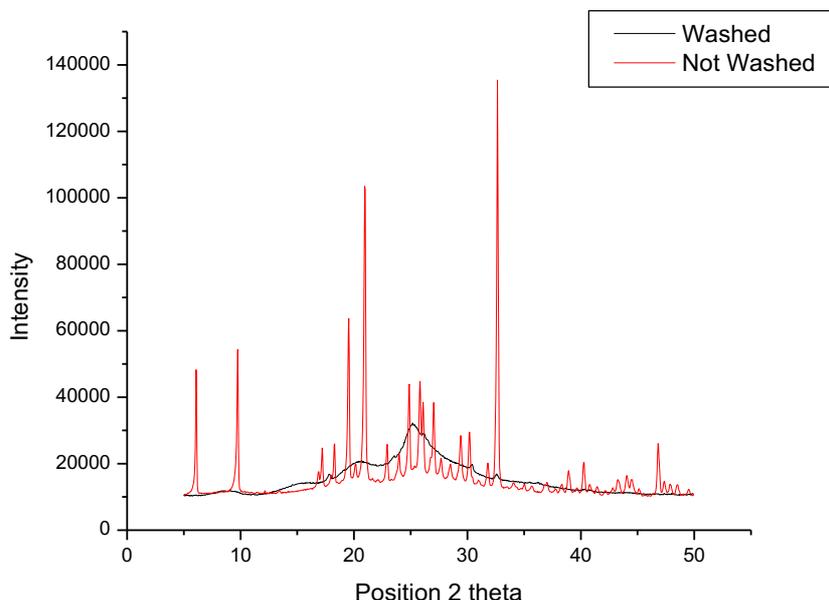
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*Figure 14: Comparison PANI 8%*

In this figure, we can see better that the effect of the conditions is not important at the molecular structure of the PANI. Under stirring and stagnant conditions we can see the same peaks with almost the same intensity but the peak that appears at  $2\theta=33^\circ$  [7] has more intensity at stirring conditions and, they show more little peaks related to impurities of PANI reaction. These impurities were removed from the reaction by the washing step but, unfortunately, the yield was not 100%.

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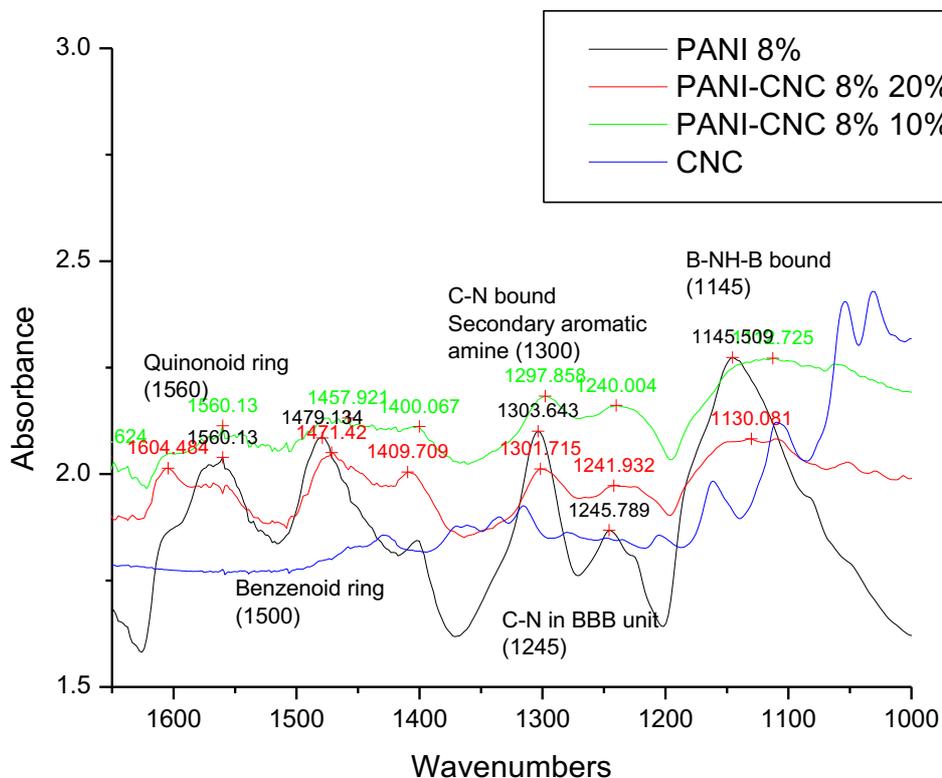
*Figure 15: Comparison PANI 8% 2 FD washed and not washed*

This plot confirms that there is a huge difference between both samples. There are a lot of peaks in the not washed sample due to the impurities of the polymerization of PANI that do not let us see the main peaks of PANI. For this reason, PANI must be washed after 24h of reaction, to remove all the impurities that can be created during the polymerization. The sample that was drying at room temperature was not characterized due to the brown particles that were found at the surface of PANI. These brown particles are aniline oligomers that did not react completely, so they can be removed thanks to the washing step.

### 3.2.2 FT-Infrared Analysis

Infrared analysis was performed to know the chemical structure of the samples. This technique will show the characteristic peaks that are related to certain chemical structures.

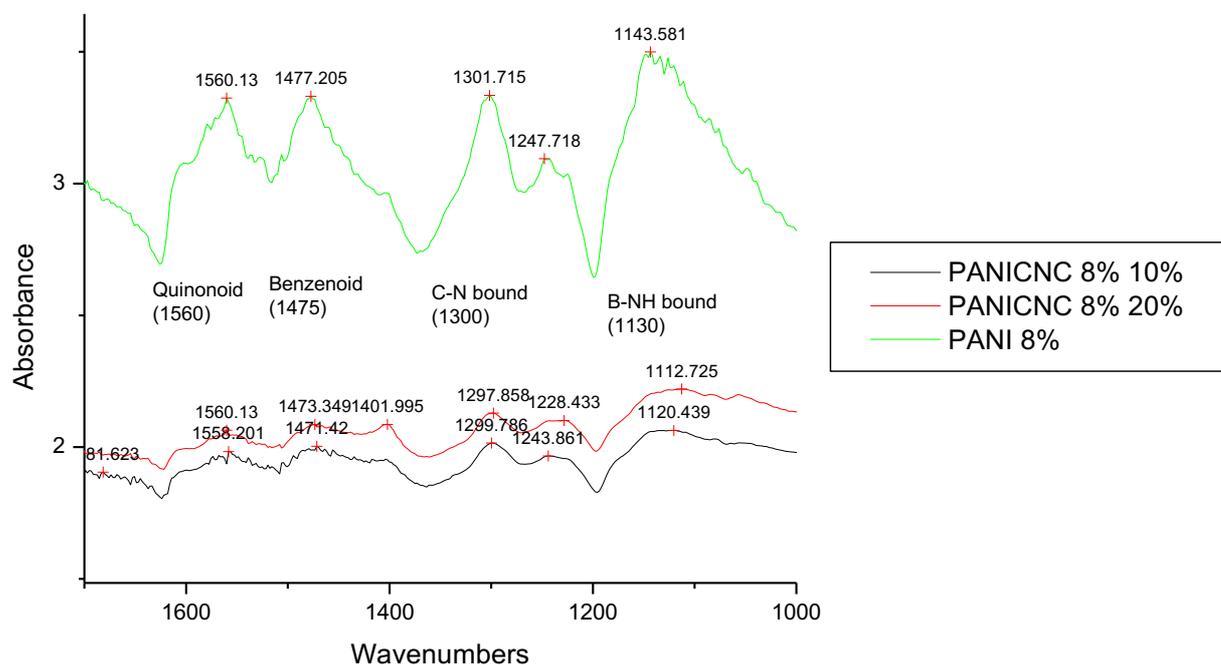
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*Figure 16: IR results for PANI 8% stagnant conditions*

If we analyze the peaks, we can see that the peaks are related to the structure of polyaniline. The characteristic peak at 1560 belongs to the quinonoid ring that is formed in the polyaniline molecule and the next one is the benzenoid ring at 1500 approximately. Other peaks are related to the C-N (1300) and benzenoid-NH (1125) bounds included in the molecule. This figure also show that is difficult to identify the peaks that belong to CNC because the solid content is too low and it exists an overlap between some peaks. [8]

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*Figure 17: IR results for PANI 8% stirring conditions*

For stirring conditions there is no change and we can see the same representative peaks of PANI in the graphics. The peaks related to Quinonoid, benzenoid and the other bound in PANI molecule has the same values. So, we can assume that there is no difference in the chemical structure despite the way that has been performed the experiment. [8]

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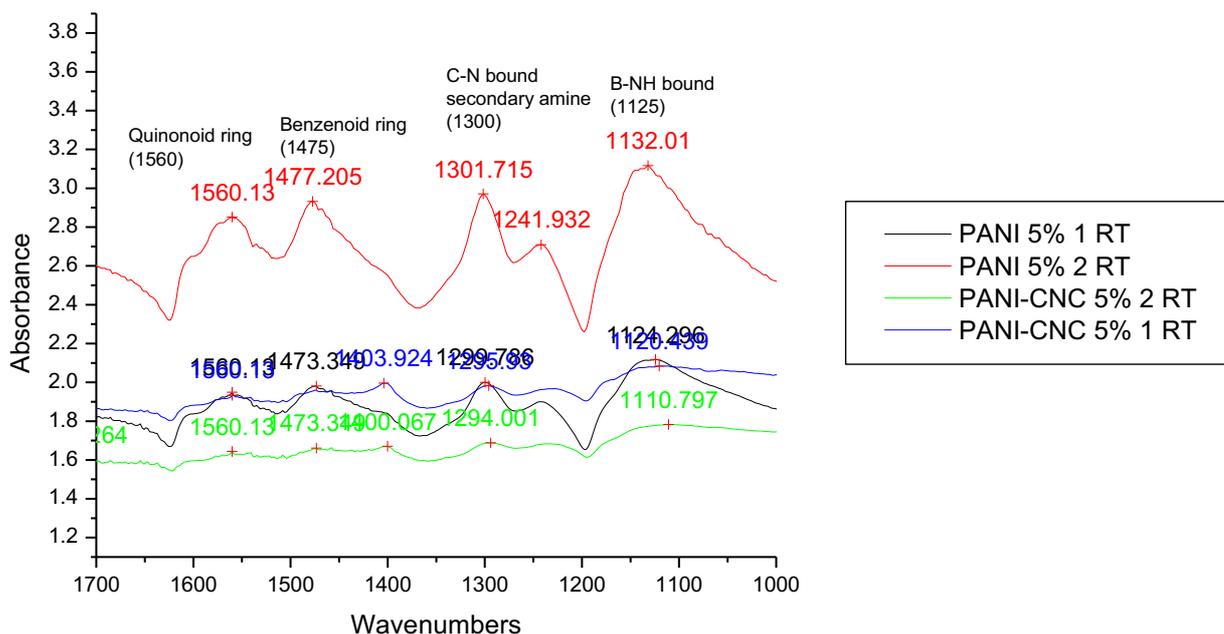


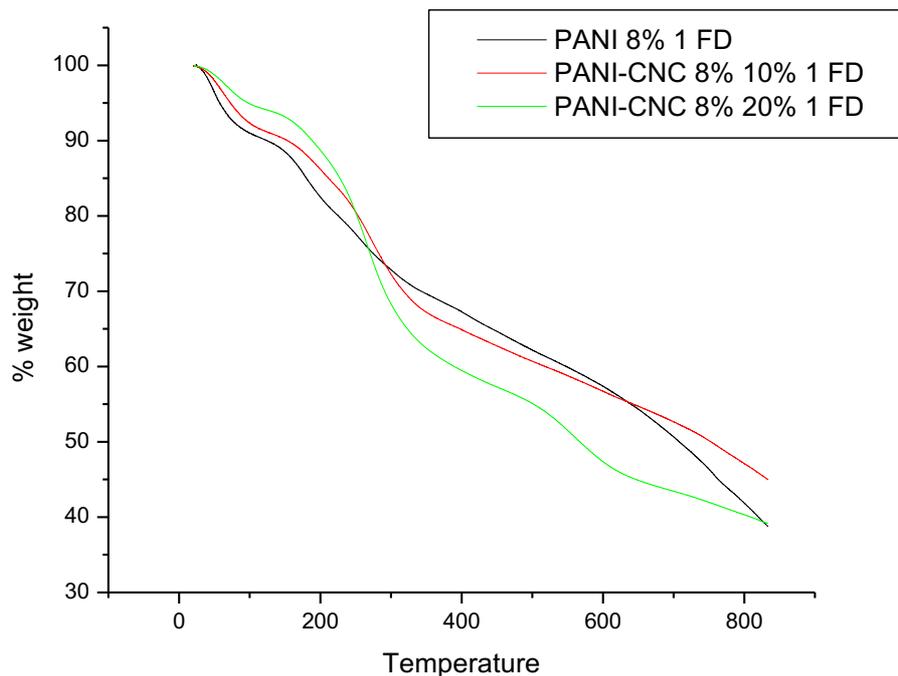
Figure 18: FT-IR analysis for PANI 5% and PANI-CNC 5%

For PANI 5% the results are very similar so it shows that the solid content does not affect the chemical structure of the PANI molecule due to the peaks has the same values.

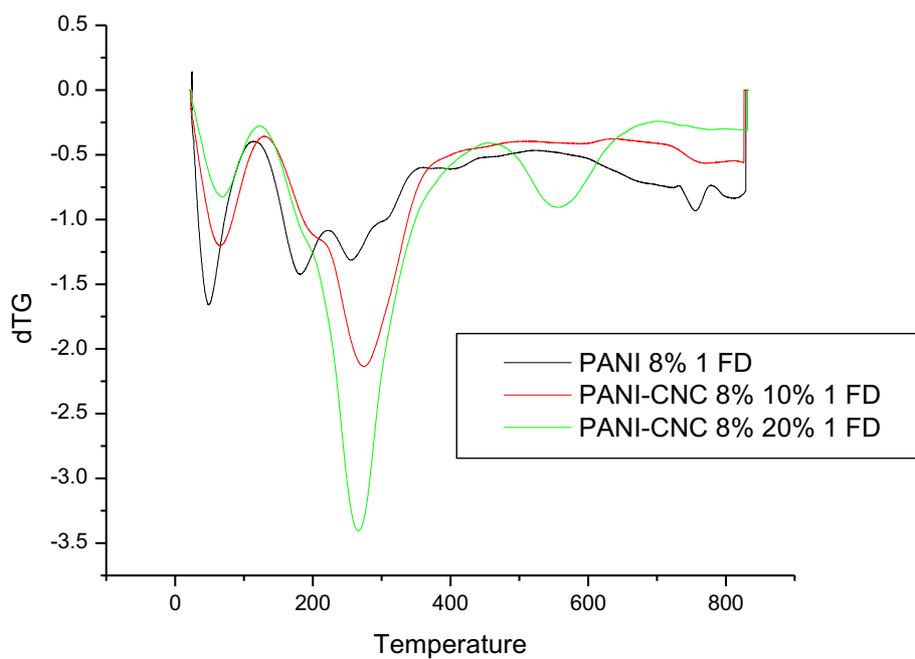
### 3.3 Thermogravimetric analysis

The thermal gravimetric analysis for this samples shows the differences when the sample has CNC. In figure 17, the thermal degradation of PANI is starting at 50°C to 120°C that is related to the moisture of the sample. Then, the second loss that occurs at 150°C to 300°C according to the decomposition of the dopant [5] that in this case is HCl. The third step that is longer than the other two because is when is happening the decomposition of PANI.

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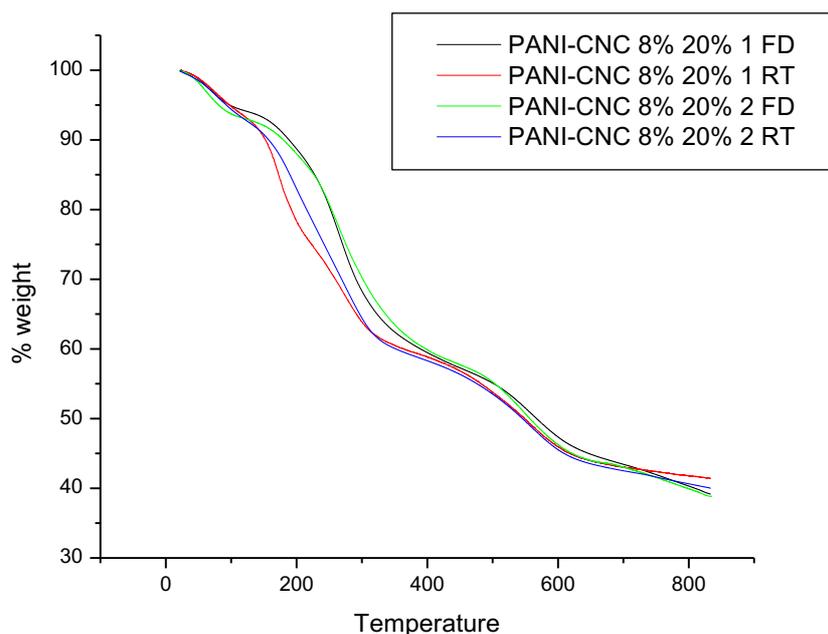
*Figure 19a: TGA characterization for PANI 8% with 10% and 20% CNC content.*



*Figure 19b: TGA characterization for PANI 8% with 10% and 20% CNC content.*

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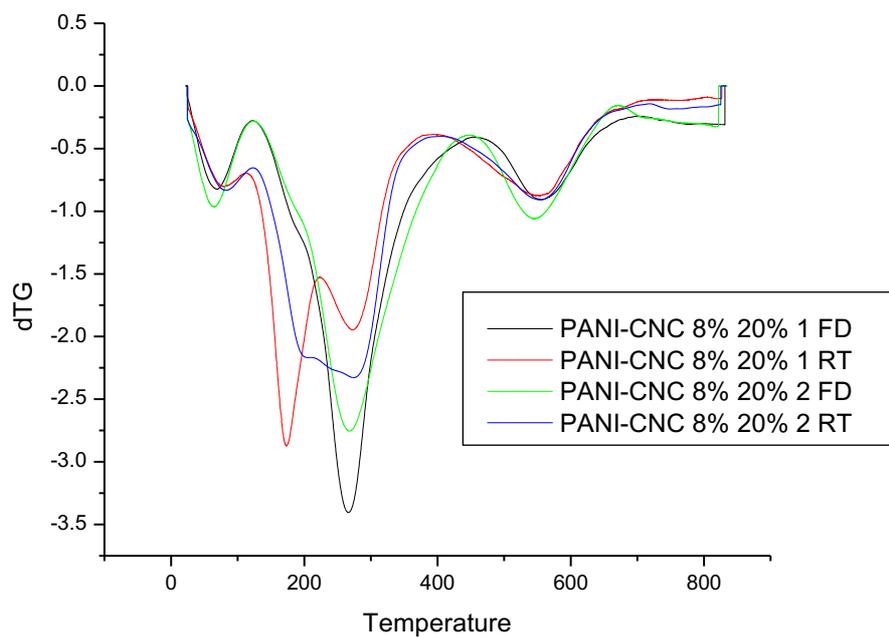
The two composite samples are like PANI sample but at the second step the losses are bigger due to the CNC content. CNC has a low thermal stability and at 160°C to 350°C starts the decomposition of the material. According to that, the losses are bigger in the sample with 20% CNC than 10% CNC as we can see in the figure. The third step is the same as the pure PANI because there are not CNC and is the final decomposition of the material.



*Figure 20a: Comparison Starring vs Stagnant and RT vs FD*

In this figure, there is a comparison with the same experiment to compare the effect of the conditions and the drying. However, all the samples have the three different degradation steps we saw in the previous figure. The first one is related to the moisture of the samples, we can see that in the room temperature samples the losses are bigger, so it means that freeze-drying can remove better the water from the sample. The second step is related to the dopant decomposition (in this case HCl) and to the decomposition of the CNC in the samples. The third step is the final step when occurs the decomposition of PANI.

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*Figure 20b: Comparison Starring vs Stagnant and RT vs FD*

*Table 1. TGA peaks*

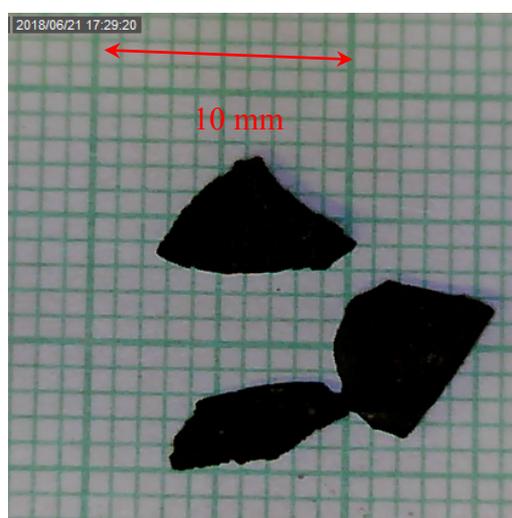
Sample	Peak (°C)			
PANI 8% 1 FD	50.06	181.91	255.28	755.7
PANI-CNC 8% 10% 1 FD	65.74	274.02		
PANI-CNC 8% 20% 1 FD	68.97	266.24	555.75	
PANI-CNC 8% 20% 1 RT	173.11	276.07	553.93	
PANI-CNC 8% 20% 2 FD	64.63	267.51	545.48	
PANI-CNC 8% 20% 1 RT	82.42	274.04	553.81	

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### 3.4 Electrical conductivity analysis

This measurement is the most important because is needed to reach a good electrical conductivity value to compete with traditional supercapacitors. There were some problems to measure the samples due to their rough particle size, which cannot feed the measuring chamber and the homogeneity of the test may not be ensured.

Problem of rough particle size; cannot be fed into the measuring chamber, and if it is successful, measurement homogeneity cannot be ensured. Since the samples are very conductive, measured at the limit of the possibilities of the current apparatus, measurement uncertainty can be expected around 10% of the measured value.



*Figure 21: Particle size of the sample (PANI 8% 1 RT)*

In this table, we can observe the electrical conductivity of the samples. Only 8% solid content and room temperature were analysed because they were small pieces enough big to do the analysis.

*Table 2: Electrical conductivity*

Sample	h(mm)	h(m)	R ( $\Omega$ )	G(S)	K(S/cm)
PANI 8% 1 RT	3,49	0,00349	4,3	0,233	0,6459
PANI 8% 2 RT	9,11	0,00911	9,2	0,109	0,78799
PANI-CNC 8% 1 10% RT	1,18	0,00118	2,7	0,37	0,348
PANI-CNC 8% 2 10% RT	3,46	0,00346	8,1	0,123	0,34
PANI-CNC 8% 1 20% RT	2,33	0,00233	67	0,0149	0,028
PANI-CNC 8% 2 20% RT	0,93	0,00093	13,8	0,072	0,054

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PANI samples are the most conductivity because the polymer is pure and its properties are not affected by CNC. CNC is not a conductive compound so when there is a small amount in the composite it makes more difficult for the electrons to move inside the composite. Due to that, we can see a decreasing of the electrical conductivity when the content of CNC is increasing.

The conductivity of the composites that contain 20% CNC solid content are 100 times less conductive than pure PANI in the same conditions.

#### 4. CONCLUSION

After the characterization of the samples to know their morphology, chemical structure, thermal and electrical conductivity analysis we can say that CNC improve the characteristics of PANI to achieve a useful film for supercapacitors.

The morphology of PANI is affected by the washing step that is redoping PANI, that as we could see in the comparison of PANI washed and not washed there are less crystalline in washed samples but also the not washed sample has a lot of impurities as we can see in SEM image and in the XRD comparison.

The chemical structure of the PANI samples does not change as we can see in FTIR analysis and in XRD graphics. There is a difference when the content of CNC is bigger in XRD graphics we can see the chemical structure of CNC confirming the presence of CNC in its crystalline form. The presence of quinonoid and benzenoid structure confirms that the PANI samples have the emeraldine chemical structure as is required for a good electrical conductivity of the composite.

The thermal stability of the composite is almost the same for all the samples that were done. PANI and CNC start to decompose at low temperature so there is no a change when CNC is added to the polymer. The graphics show similar behaviours for all the composites despite the way that was made.

The values of the electrical conductivity of the samples are decreasing with the increasing of CNC solid content. This was expected due to the lack of CNC electrical properties because its chemical structure. Besides, the low electrical conductivity of the samples with 20% CNC solid content makes this composite worse than the traditional supercapacitors. So, the best PANI-CNC composite should be between 10% and 20% CNC solid content to have a good electrical conductivity for the uses that are needed.

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## 5. REFERENCES

1. S. Rebouillat and F. Pla, "State of the Art Manufacturing and Engineering of Nanocellulose: A Review of Available Data and Industrial Applications," *Journal of Biomaterials and Nanobiotechnology*, Vol. 4 No. 2, 2013, pp. 165-188.
2. Hassouna F, Korbel' a'rov'a J, Jaquet B, Kutorglo EM, Kopeck' y D, Ulbrich P, Fulem M, Hrdli'cka Z, 'So' o's M, *An environmentally benign methodology to elaborating polymer nanocomposites with tunable properties using core-shell nanoparticles and cellulose nanocrystals*, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* (2018)
3. Shumakovich, G. P, Morozova, O. V, Khlupova, M. E, Vasil'eva, I. S, Zaitseva, E. A, & Yarapolov, A. I. (2017). *Enhanced performance of a flexible supercapacitor due to a combination of the pseudocapacitances of both a PANI/MWCNT composite electrode and a gel polymer redox electrolyte*. *RSC Advances*, 7, 25191-25198. doi:10.1039/c7ra03379f
4. Zheng, W., Na, B., Liu, H., Jin, T., & Yuan, D. (2017). *Nanocellulose-mediated hybrid polyaniline electrodes for high performance flexible supercapacitors†*. *RSC Advances*, 7, 12969-12976. doi:10.1039/c7ta01990d
5. Sinha, S., Bhadra, S., & Khastgir, D. (2009). *Effect of Dopant Type on the Properties of Polyaniline*. *Journal of Applied Polymer Science*, 112, 3135-3140. doi:10.1002/app.29708
6. H. Wei, K. Rodriguez, S. Renneckar, W. Lenga and P. J. Vikesland, *Analyst*, 2015, 140, 5640-5649
7. R. L. Razalli, M M. Abdi, P. M. Tahir A. Moradbak, Y. Sulaiman and L. Y. Hengc *RSC Adv.*, 2017, 7, 25191-25198
8. M. Trchová† and J. Stejskal, *Pure Appl. Chem.*, Vol. 83, No. 10, pp. 1803–1817, 2011.
9. J. Joo, H. G. Song, Y. C. Chung, J. S. Baeck, S. K. Jeong, J. S. Suh and E. J. Oh *Journal of the Korean Physical Society*, Vol. 30, No. 2, April 1997, pp. 230-236
10. Y. Habibi, *Chem. Soc. Rev.*, 2014, Vol 43, pp. 1519-1542
11. Z. Wang, D. O. Carlsson, P. Tammela, K. Hua, P. Zhang, L. Nyholm, and M. Strømme, 2015, Vol. 9, No. 7, pp 7563-7571