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Trabajo Final de Grado

Study on synthesis, surface derivatization, processing and techno-economic analysis of a PLA – Nanocellulose composite

Estudio en la síntesis, derivatización superficial, procesado y análisis tecno-económico de un compuesto de PLA - Nanocelulosa

Gustavo Geraldo Silva
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Do what you can, with what you have, where you are.

Theodore Roosevelt

During times of distress, the best of human nature comes to show. This is not how I imagined my 5 years of Materials Engineering would conclude, nor did I expect to hand in my Final Degree Work in such a manner. However, **the only limitations to science are the ones we impose on ourselves as a civilization**. Despite not being able to conclude the experimental work I initially planned on doing because of the restrictions imposed by the COVID-19 pandemic, with this work I intend to shed more light into utilizing cellulose as a sustainable means of increasing the mass adoption of PLA, thus contributing in some way to accelerating the transition to global sustainability. During those times of uncertainty, I am thankful for my fellow colleagues and supervisors who have shown an astounding supportiveness and flexibility in helping me conclude this work. I am especially thankful for **Raisha Garcia**, **Noemi Gavieiro** and **Javier Fernandez** who have promptly helped me in any doubt and have oriented me in going about the best options to carry out this work.

I am also thankful for the flexibility and rigor shown by the whole Faculty of Chemistry and the professors of the Department of Materials Science and Physical Chemistry. Over those years, I've learned from each professor in a close-knit matter and I can truly affirm to have made the knowledge I learned from them my own. In special, I thank my tutor **Elena Xuriguera** who has accompanied and mentored me over those years, and to whom I'll be forever thankful.

Finally, I thank my mom, **Claudia Aparecida Silva**, for her love and her sacrifice as we migrated to Spain back in 2007. Without her sacrifice and spirit of endeavor, I would have never had the opportunity of concluding this work and my Degree in such a renowned University. I owe it all to her and to our Lord and Savior **Jesus Christ**, whose abundant mercy and blessings have never left me lost or without hope.

REPORT

Contents

1. GLOSSARY

AFM: Atomic Force Microscopy

BC: Bacterial Cellulose

CNC: Cellulose Nanocrystals

CNF: Cellulose Nanofibers

CNW: Cellulose Nanowhiskers

DSC: Differential Scanning Calorimetry

EDS: Energy Dispersive Spectroscopy

FESEM: Field Emission Scanning Electron Microscopy

FTIR: Fourier Transform Infrared Spectroscopy

MCF: Mineralized Collagen Nanofiber

MPSP: Most Probable Selling Price

NMMO: N-Methylmorpholine N-oxide

PE: Polyethylene

PET: Polyethylene Terephthalate

PGA: Polyglycolic acid

PLA: Polylactic Acid

PP: Polypropylene

PS: Polystyrene

SEM: Scanning Electron Microscopy

TEM: Transmission Electron Microscopy

TEMPO: 2,2,6,6- tetramethylpiperidine-1-oxyl radical

XPS: X-Ray Photoelectron Spectroscopy

2. SUMMARY

As a biodegradable material that can be obtained from sustainable resources, Polylactic acid (PLA) has positioned itself among one of the most prominent materials to substitute petrochemical-based plastics in our quest towards a circular, carbon-neutral economy. On the other hand, Cellulose, a natural polymer found as a reinforcement element in plants, cells and tissue, has a proven record of use not only as paper, but also in many composite applications as a thickening agent, as a binder, or as reinforcement in composite materials.

Despite its great prospects, PLA has some serious drawbacks in its mass adoption as a substitute material of mainstream olefins, mainly due to its relatively poor mechanical, thermal and permeability properties. As such, Cellulose, in particular that which is sourced from agricultural waste products, such as Soy Husks, and scaled to its nano-constituent particles, has the potential to be used as a reinforcement and filler material in PLA, improving its weak properties. However, due to their different surface behavior, a mixture of PLA and Nanocellulose is hard to achieve without special processes.

The goal of this final degree project is to study the processes in place to individualize the different nano-constituents of Cellulose, namely Cellulose Nanofibers (CNF), modify its surface behavior to make it compatible to PLA and explore the processes to which a PLA – Nanocellulose composite could be produced. This study has been made based on existing bibliography from other research fellows and the most prominent pathway to a PLA – Nanocellulose composite has been presented on this study along with a techno-economic analysis of its viability.

3. RESUMEN

Como un material biodegradable capaz de obtenerse de fuentes sostenibles, el Ácido Poliláctico (PLA) ha ganado una reputación como uno de los materiales más prominentes para sustituir los plásticos petroquímicos en la marcha hacia una economía circular neutra en emisiones de carbono. Por otro lado, la Celulosa, un polímero natural encontrado como elemento de refuerzo en plantas, células y tejidos, tiene un pasado demostrado en su uso no solo como papel, sino también en muchas aplicaciones compuestas como un agente espesor, aglomerante o como refuerzo en materiales compuestos.

A pesar de sus buenos prospectos, el PLA tiene serias desventajas en su adopción en masa como un material sustitutivo a las olefinas comunes, principalmente debido a sus relativamente malas propiedades mecánicas, térmicas y de permeabilidad. Como tal, la Celulosa, en particular aquella proveniente de desechos de la agricultura, como las Cáscaras de Soja, y escalada a sus partículas nano-constituyentes, tiene el potencial de ser usada como un material de refuerzo en el PLA, mejorando sus malas propiedades. Sin embargo, debido a sus diferentes comportamientos en superficie, es difícil de lograr una mezcla de PLA y nanocelulosa sin llevar a cabo unos procesos especiales.

El objetivo de este trabajo fin de grado es estudiar los procesos existentes para individualizar los diferentes nano-constituyentes de la Celulosa, en particular las Nanofibras de celulosa (CNF), modificar su comportamiento superficial para hacerla compatible con el PLA y explorar los procesos por los cuales se pueda producir un material compuesto de PLA – Nanocelulosa. Este estudio se ha hecho basado en bibliografía existente de otros grupos de investigación y el camino más prominente a producir un compuesto de PLA – Nanocelulosa se ha presentado en este estudio junto con un análisis tecno-económico de su viabilidad.

4. ORIGINS

In previous years, there had been multiple studies on how the use of cellulose and its derivatives can improve the functional properties of one of the most sustainable plastics by excellence, Polylactic acid (PLA), since its inherent properties, such as rigidness or thermal degradability inhibit its widespread use in fields such as those of biomedical prothesis or packaging products [1]–[4].

For instance, according to Scopus database search results, there are 5,646 documents with the keyword "PLA Composite", a trend that has boomed since the early 2000's, as shown in Figure 1. Equally, the search for the keywork "Cellulose Composite" yielded similar trends, with a total number of 16,422 articles found. Nonetheless, despite showing similar trends, a much smaller number of articles is found for the keyword "PLA Cellulose", for a total of 1,186 articles. Therefore, it can be inferred that the particular field of creating PLA composites is trendy, and that more research can be done in the field of PLA – Cellulose composites.
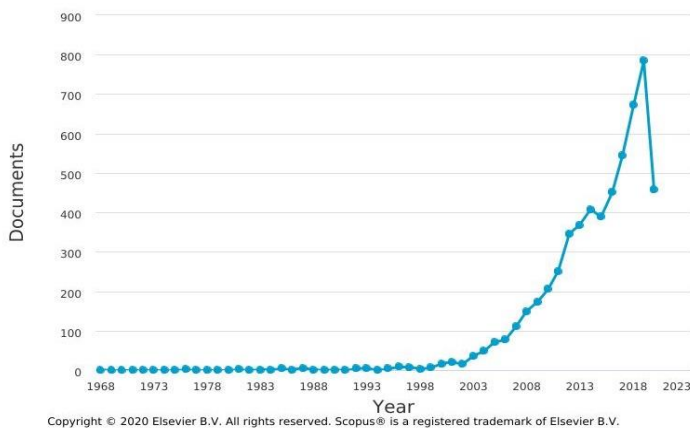
Figure 1: Number of documents published by year with the matching keyword "PLA Composite". Source: Scopus Document Search.

In 2019, Anna Vilche studied the possibility of obtaining nanocellulose from Soy Husks, a high cellulose-content food industry residue, via a chemical acid hydrolysis treatment, then subsequently electrospinning a solution of the cellulose product and a PLA/Polyglycolic acid (PGA) copolymer dissolved in acetone [5]. However, it was reported that the procedure couldn't yield individualized nanocellulose fibers and neither produced a PLA - Nanocellulose composite, which was attributed to cellulose particle agglomeration and a source of PLA with a high molecular weight, which hindered the solubility of the polymer.

5. INTRODUCTION

As a biodegradable plastic, over the years PLA has shown to have potential applications across a wide range of fields [6]. Among those, are the general packaging applications such as food boxes or plastic cups and a multitude of fibers used in textile and medical applications [7]–[9]. In Europe, these applications represent a whopping 38% of the consumption of olefinic plastics such as Polyethylene Terephthalate (PET), Polyethylene (PE), Polystyrene (PS) and others [10]. Additionally, thanks to its biodegradability properties, not only can PLA revolutionize whole industries by improving our responsibility towards the environment [11], but also yield interesting applications in the medical field as a scaffold in tissue generation or as a structural material for bone prothesis [12]–[16].

One of the greatest challenges we face with using PLA massively is its costly price [6]. Despite showing an annual demand growth that is estimated to double every 3-4 years, the precursor for producing PLA, lactic acid, is still extracted to a great extent from intensive crops, thus entering in direct competition with the food industry, which drastically increases its purchase and processing costs in comparison to traditional plastics [17].

Another great challenge from using PLA is its mechanical properties. Its compositional structure yields a very fragile plastic, requiring an extensive use of plasticizers, which in turn yield inferior permeability or mechanical properties in comparison to traditional plastics in applications such as in the packaging industry (Figure 2) and in comparison to other metals in the field of medical prosthesis (Figure 3). Moreover, its biodegradability makes it very susceptible to water swelling, making PLA a suboptimal alternative as a gas/liquid barrier or as a material resistant to thermal degradation [17].

Thankfully, it was shown that the addition of nanoparticles to the bulk of PLA, such as nanosilicates, considerably improves its mechanical properties and thermocompositional stability [18], [19]. There are numerous nanoparticles that can play a different role in improving specific characteristics of PLA applications, but there are still many challenges

to overcome in processing PLA composites [20]. One such nanoparticle candidate is nanocellulose and its derivatives [21], which is the focus of this study.
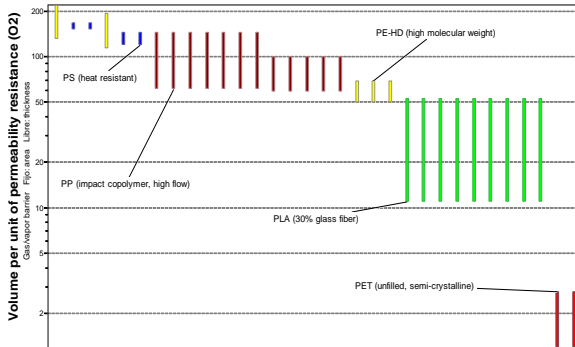
Figure 2: Comparative chart depicting the material permeability index of different polymers used in packaging optimized to minimum. Source: GRANTA Edupack.

Figure 3: Comparative chart depicting Young's modulus versus Yield Strength of different materials utilized in prosthetics applications. Source: GRANTA Edupack

The advantages of using nanostructured cellulose in improving the properties of PLA are many; for one, like PLA, cellulose comes from biological, sustainable sources, and because of its inherent biocompatibility, low density and high surface area, with hydroxyl

groups easily modifiable for adapting it to different applications, nanocellulose is an ideal candidate for its industrial use [22].

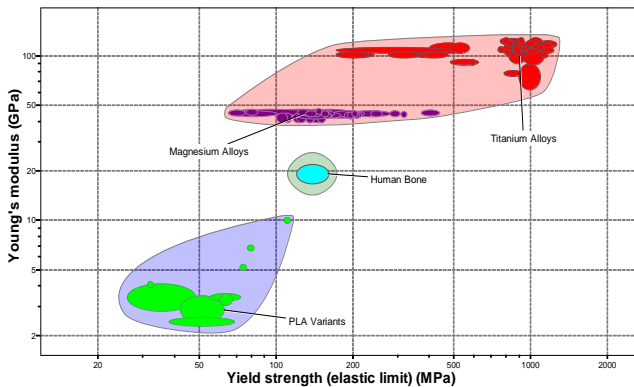There are many nanocellulose synthesis methods, which vary depending on the cellulose source and its desired physical properties [23]–[26]. Nowadays, these methods are fairly optimized, and are able to yield different types of nanocelluloses, such as crystalline nanocellulose (CNC) via acid hydrolysis [27], cellulose nanowhiskers (CNW) via acid hydrolysis and lyophilization [28], or cellulose nanofibers (CNF), via a physical-chemical fiber individualization treatment mediated by 2,2,6,6-tetramethylpiperidinyl-1-oxyl (TEMPO) as a catalyzer in the oxidation of some of the hydroxyl groups in the cellulose structure [29].

Nonetheless, the greatest challenge is achieving a homogenous mixture and physical-chemical bonding of nanoderivative celluloses with the PLA matrix, since the different surface polarity of the two materials; hydrophobic in the case of PLA and hydrophilic in the case of cellulose, hinders surface interaction between the two materials and prevent a homogenous dispersion, thus inhibiting the cellulose from effectively reinforcing the PLA matrix [30], [31].

5.1 OBJECTIVES

Among the possible difficulties cited by previous authors in obtaining a PLA – Nanocellulose composite were a poor interaction of the solvent used to mix nanocellulose with PLA. For that reason, the scope of this study will be to compile bibliography that studies:

a)   The properties of cellulose and those particular properties critical for obtaining individualized nanocellulose fibers.

b)   The variables that affect the interaction of nanocelluloses with PLA and other solvents and the existing surface modification processes that can alter these interactions.

With much regret, as of the date of this writing, the world is submerged in one of the greatest health crises of modern civilization, the COVID-19 pandemic. As a result, all on-

site academic and research activities have been suspended, precluding the execution of the experimental part of this project, which consisted in:

a) Experimentally evaluating the different nanocellulose obtainment methods and characterizing its morphological, thermal, compositional and rheological properties with the Field Emission Scanning Electron Microscopy (FESEM) + Energy Dispersive Spectroscopy (EDS), Differential Scanning Calorimetry (DSC), Fourier Transform Infrared Spectroscopy (FTIR) and Vibrational Viscosity techniques, respectively.

b) Experimentally evaluating the different obtainment techniques of a PLA polymer filled with different types of nanocellulose and its rheological properties in regard to the production of hydrogels or in regard to the production of filament for extruder-based 3D printers, along with the final mechanical properties obtained through each processing technique.

However, as an alternative, aside from exploring all the bibliography mentioned earlier, an experimental design for obtaining a PLA - Nanocellulose composite will also be proposed, along with a techno-economic analysis of each proposed design. Additionally, different routes for improvement will also be proposed in order to continue the study experimentally if conditions caused by the COVID-19 pandemic are alleviated.

6. CHARACTERISTICS OF CELLULOSE, CHALLENGES OF ITS USE IN COMPOSITE MATERIALS AND EXISTING SOLUTIONS

Cellulose is a polymeric fiber composed by a chain of polysaccharide monomers which act as a structural component in a variety of natural structures, specifically those of vegetal forms of life. It's the element that shapes the walls of cells and gives mechanical strength to the trunk of trees. In a vegetal structure, cellulose acts analogously to a fiber that reinforces a polymeric resin matrix. In the case of vegetal structures, such resin is called lignin, which acts as a binder of the cellulosic fibers, as shown at Figure 4. Each fiber is composed by different cellulose microfibers, binded together by hemicellulose, a more amorphous derivative of cellulose. The microfibers are the most basic structure of cellulose, in which thanks to its hydrogen bonds, the whole structure is able to conform to crystalline segments united by amorphous segments [32].
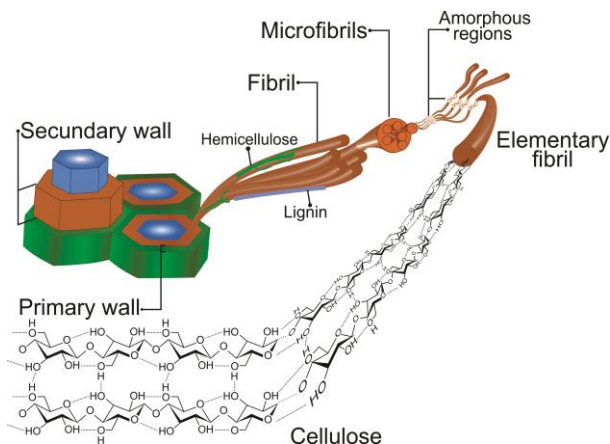

Figure 4: Hierarchical structure of cellulose in vegetal structures. Credit: Mhd Abd Cader Mhd Haniffa et al. Department of Mechanical Engineering, Faculty of Engineering, University of Malaya.

In cellulose processing industries, like that of paper, compounds like hemicellulose or lignin are eliminated via different processes in order to achieve a high-purity cellulose pulp, with which its many applications are conformed from. For instance, in the paper industry, the pulp is dried and roll-conformed and as the drying process occurs the hydrogen bonds between cellulose microfibrils hold together the bulk structure [33].

What gives cellulose fibers their excellent mechanical properties is their molecular structure. Such structure is reflected on Figure 5, which depicts the lineal conformation of this homopolymer in which the β-D-glucopyranosyl groups attached to the C1 and C4 carbon atoms provide the molecular union, whereas the primary and secondary hydroxyl groups in the C2, C5 and C6 positions allow the creation of hydrogen bongs between molecules which, similarly to other polymers, results in crystalline conformations [34].
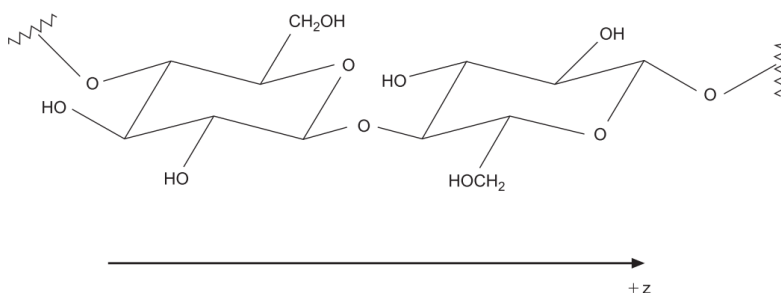

Figure 5: Molecular structure of cellulose. Credit: ANTOINETTE C. O'SULLIVAN, Department of Chemistry and School of Agriculture and Forestry Sciences, University of Wales

Depending on the source of cellulose, those molecules result in a wide polymerization degree range, which in sources like wood, could be around 10000 units and in sources like cotton, could be around 15000 units [34].

Like in most polymers, the polymerization process of cellulose is far from being completely understood, since there is evidence that the hydrogen bonds of these long chains help them shape into a monoclinic crystal structure that has different crystalline phases of stability. This crystal structure has some crystalline segments and other much shorter amorphous segments. These vary depending on the source and Temperature-Pressure conditions of cellulose. This makes a total understanding of the molecular structure of cellulose difficult to attain.

6.1.   MODIFICATION OF THE HYDROXYL GROUPS IN IMPROVING CELLULOSE INTERACTION WITH SOLVENTS

Because of the hydroxyl groups in its molecular composition, cellulose can conform to high-strength tridimensional crystalline structures. Nonetheless, the large bond forces between these groups packs cellulose molecules tridimensionally and hinders the access of solvents to the structure [35]. Another factor that hinders the interaction of solvents with cellulose is the position of these hydroxyl groups. As shown in Figure 6, hydroxyl groups occupy equatorial positions in the molecule, whereas C-H ring groups occupy the axial positions. This gives the molecules a hydrophilic character in the equatorial region and hydrophobic character in the axial region.
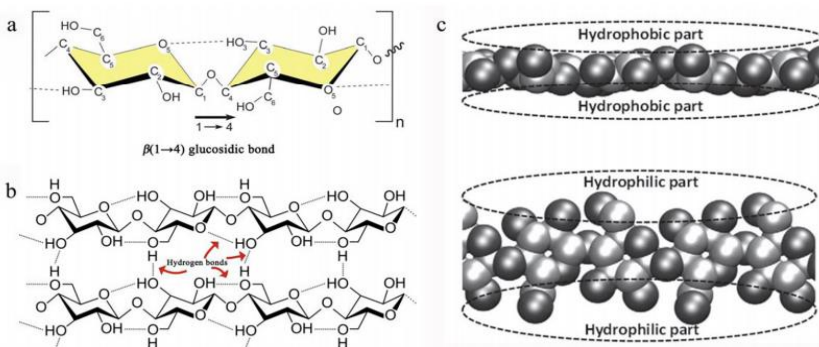

Figure 6: Depictions of the cellulose repeating unit (a) intra- and inter chain of hydrogen bonds in the 3D structure (b) and representation of axial and equatorial hydrophobic/hydrophilic interactions in cellulose (c). Credit: Bruno Medronho et al. IBB-CGB, Faculty of Sciences Technology Ed. 8, University of Algarve. Faro, Portugal

This is a problem because the majority of polymer reinforcement mixture processes are based on dissolving both filler and matrix in a common solvent in order to achieve a homogenous mixture between the two. The ability of having an easily solution-dispersible cellulose opens the door for not only homogenously reinforcing polymers in a common solution, but also creating cellulose hydrogels with a host of applications, such as in the electronics industry as an ion-conducting membrane for next-generation lithium-ion batteries [36], or in the biomedical industry by 3D printing cellulose tissue-growing scaffolds [37].

Therefore, in order to succeed dissolving cellulose, the consensual position of experts in the field revolves around routes that can partially or completely break the hydrogen bonds that form in the tridimensional structure of cellulose, thus allowing individual cellulose crystals or molecules to be individualized [38]. Of all the routes available, two major routes can be categorized: the derivative and non-derivative routes [39].

6.1.1. Derivative cellulose modification routes – TEMPO-mediated oxidation

Derivative routes consist on modifying the hydroxyl functional groups, substituting those for other groups, usually carboxymethyl groups, in order to break the tridimensionality created by hydrogen bonds [40]. The first derivative ever produced was nitrocellulose, in 1845, which allowed cellulose to be dissolved in alcohol and acetate solvents for the first time [41]. Another greatly utilized route was of that of cellulosic xanthates [42].

Nowadays, one of the most promising derivative routes is the partial oxidation of cellulose crystals mediated by the radical TEMPO [36], that yields carboxymethylcellulose (CMC), a derivative of cellulose characterized by having some, or all of its hydroxyl groups substituted by carboxymethyl groups, as shown in Figure 7.
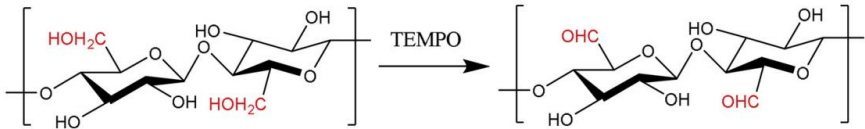
Figure 7: Structure of carboxymethylcellulose repeating unit obtained by TEMPO-mediated oxidation of cellulose. Credit: Chenghao Huang et al. State Key Laboratory for Hubei New Textile Materials and Advanced Processing Technology, College of Materials Science & Engineering, Wuhan Textile University

By having the ability of conserving a smaller proportion of hydroxyl groups on its surface microfibrils, CMC can be more readily dissolved and individualized to CNFs without completely breaking its ability to conform to a crystalline structure [43]. However, exerting such control is one of the greatest challenges of derivative routes such as that of TEMPO-mediated oxidation, because an excessive oxidation can not only modify the surface hydroxyl groups but also produce active free radicals that could break β-D-glucopyranosyl bonds, which negatively affect desired characteristics from nanocelluloses, such as the degree of polymerization or the ability of forming a crystalline structure [44].

To mediate this difficulty, Isogai et al. [29], [45] have created a process in which a TEMPO/NaClO/NaClO$_2$ system is used, whose catalytic route is portrayed in Figure 8, in which a smaller reduction in the degree of polymerization was accomplished, thus maintaining a longer-chained, higher-yield nanofibrillated cellulose structure. The process consists in oxidizing 1 g of cellulose in suspension previously bleached by the Kraft process and mechanically fibrillated in a 0,1M sodium phosphate buffer solution with a pH of 6,8 and in the presence of 0,1 mmol of 4-H-TEMPO, 10 mmol of NaClO$_2$ and 1 mmol of NaClO at 40-60 ºC during 6-72 h [46].

With this process, a surface oxidized CNF was obtained, as illustrated in Figure 9. This surface modification hindered the formation of hydrogen bonds between nanofibers, which allowed the individualization of CNFs through mechanical disintegration by using an ultrasonic homogenizer or simply a household blender over a period of 2-10 minutes.

Depending on the reaction time, as shown in Figure 10, the content of carboxylate groups produced by the oxidation is different. The advantage to a higher degree of oxidation is a greater ease of nanofiber individualization, which can go as far as yielding a completely transparent solution from carboxylate contents greater than 1.5 mmol/g of cellulose (Figure 11).

Upon analyzing in a Transmission Electron Microscope (TEM) the samples obtained through this route after mechanical individualization, fibers of longitude between 20-40 μm with diameters of just 3-4 nm were observed, equivalent to crystalline cellulose fibrils built by an equivalent of just 30-40 individual polysaccharide chains.
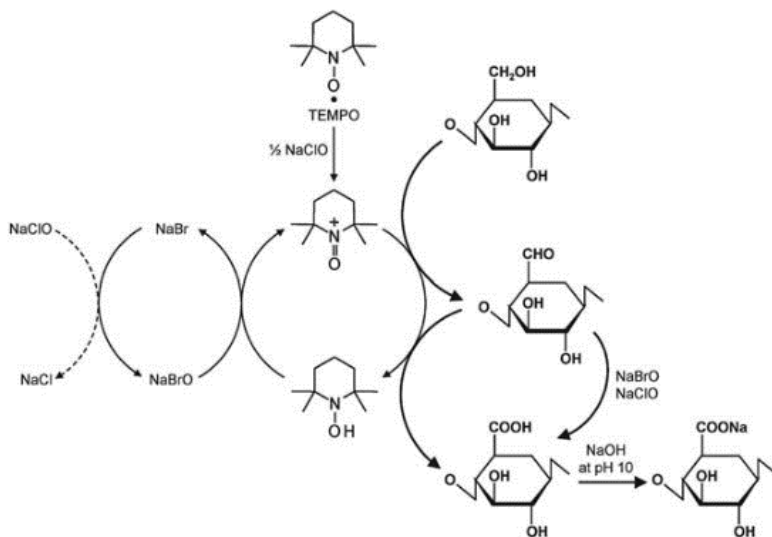
Figure 8: TEMPO-mediated selective oxidation of C6 primary hydroxyl groups of cellulose by a TEMPO/NaClO/NaBr/water system at pH 10. Credit: Akira Isogai, Tsuguyuki Saito and Hayaka Fukuzumi. Department of Biomaterial Sciences, The University of Tokyo.
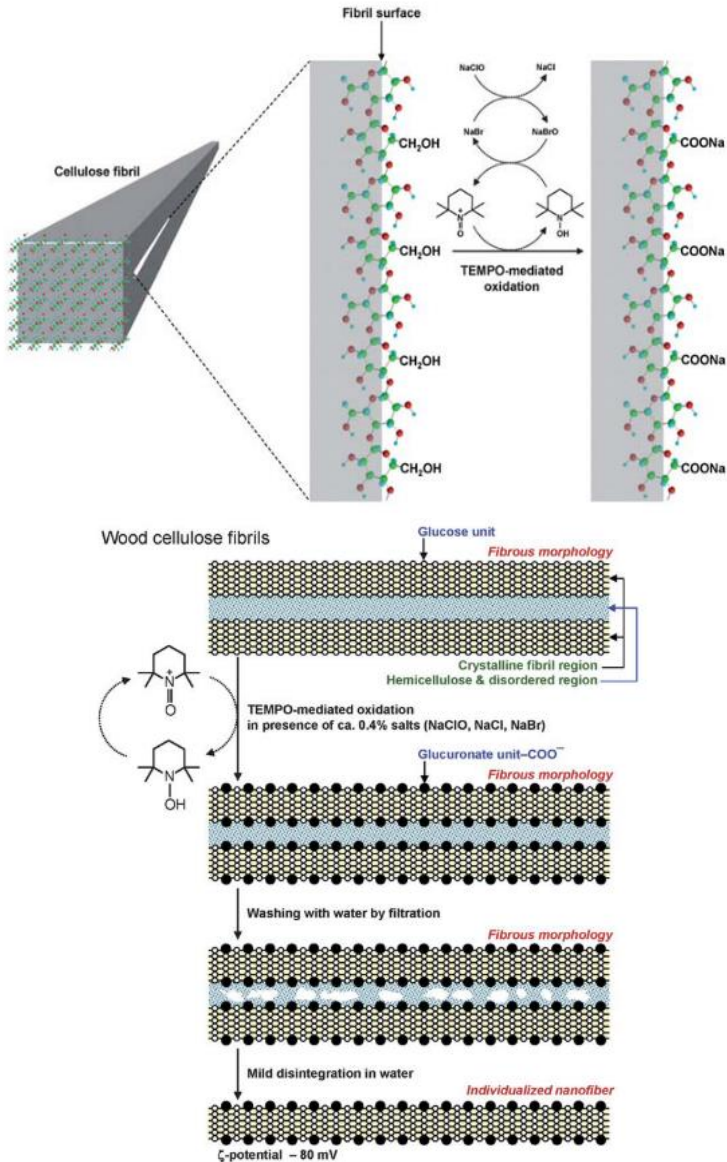
Figure 9: Schematization of surface oxidation of hydroxyl groups mediated by TEMPO (top) and the ability of individualizing, through means of mechanical desintegration, individual cellulose nanofibers (bottom). Credit: Akira Isogai et al. Department of Biomaterial Sciences, The University of Tokyo
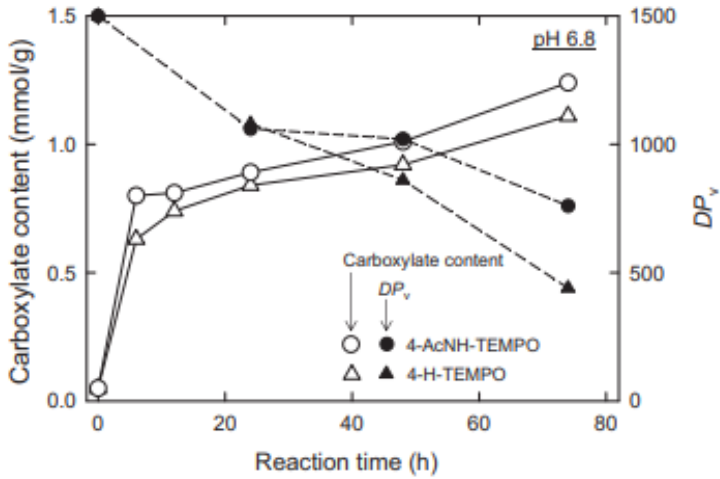
Figure 10: Carboxylate content as a function oxidation time for the system
TEMPO/NaClO/NaClO2 at 60ºC. Credit: Akira Isogai et al. Department of Biomaterial
Sciences, The University of Tokyo
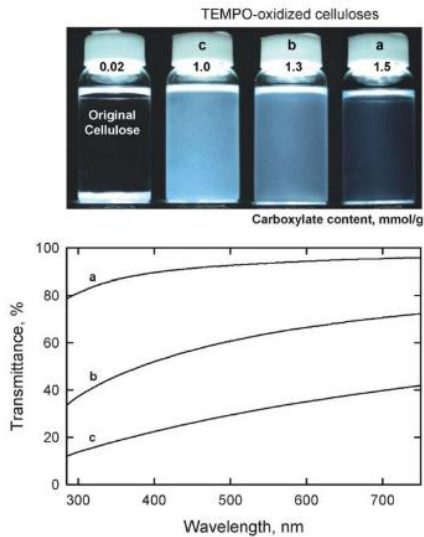
Figure 11: Transmittance of TEMPO-mediated oxidized cellulose solutions as a function of
carboxylate content. Credit: Akira Isogai et al. Department of Biomaterial Sciences, The
University of Tokyo

One example of application of TEMPO-mediated oxidation is the production of a CMC conformed to a hydrogel reticulated with nanoclay particles [47]. In this example, Jiaxin Wei et al utilized the side-metabolism cellulose product of the bacteria Acetobacter xylinum, and the role of the nanoclay used, Laponite, alongside with Ca^{2+} ions is to act as a cross-linker in gelating the bacteria-based CMC sol.

In the depiction of Figure 12, the addition of Sodium Alginate (SA) enhances cell proliferation on the substrate. The addition of $CaCl_2$ previous to 3D extruding the sol acts as a pre-gelation step, improving the rheological properties of the sol. In the study, the authors reported a thixotropic behavior of the gel extruded, with a viscosity sufficiently high for the extruded gel to maintain its own shape upon printing, and by adding Laponite, Jiaxin Wei et al obtained a smaller degree of swelling as to minimize shape distortions upon solvent extraction. Once printed, the object was submerged in a 1 wt% $CaCl_2$ solution to complete the gelation process. Following gelation, the aqueous solvent was extracted by a freeze-drying process. With that methodology, a scaffold which showed a compressibility modulus of 270 kPa and a high flexibility which was similar to that of human cartilage was obtained.

Figure 12: Schematization of hydrogel formation of TEMPO-oxidized bacterial cellulose (TOBC). Credit: Jiaxin Wei et al. State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University

6.1.2. Non-derivative cellulose modification routes – NMMO Dissolution

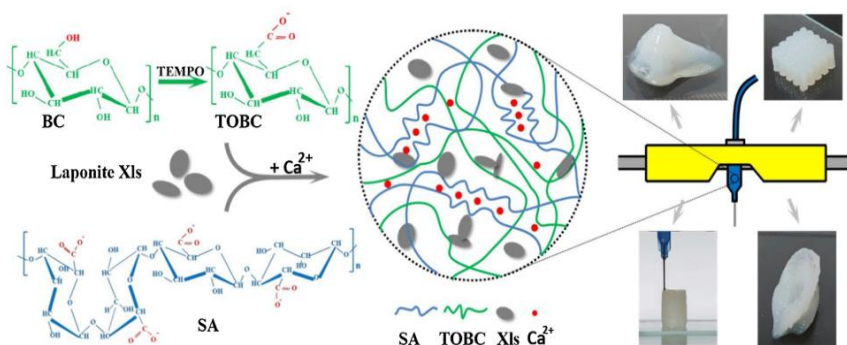In regards to the non-derivative routes to dissolving cellulose in a solution, 3 different mechanisms currently prevail; those of complexing-agent aqueous systems, those of alkaline aqueous systems and those of non-aqueous systems [35]. Of those, the route with most interest of study for this study is the route of nonaqueous systems, since because of the hydrophobic character of PLA, we wouldn't be able to form a hydrogel mixture of PLA and nanocellulose with water as a solvent.

Within non-aqueous systems, there are many interesting ways to approach the problem of dissolving cellulose, such as that of using ionic solvents based off anions like Cl- and an organic high molecular weight cation. Nevertheless, for polymer mixtures, the systems most frequently used are those based off N-methylmorpholine-N-oxide (NMMO).

The main advantage of NMMO is that it's a reagent known for breaking hydrogen bonds by electrostatic interactions, that is, without destroying the hydroxyl groups of cellulose. Moreover, it's a widely used industrial reagent for producing Lyocell fibers and can be easily recycled with recovery yields of over 99% [48]. Additionally, another advantage of NMMO is that it is soluble not only in water, but also in other polar organic solvents such as acetone, alcohols or ethers [49].

In the aqueous system, it was observed that the water concentration used to dissolve cellulose greatly affects both the dissolution mechanism as well as the morphology of the final cellulose obtained [50]. For a narrow water percentage range, of 17 – 20 %, the system jumps from yielding phase I cellulose, characterized by directional and ordered crystals, to a phase II cellulose, characterized by being amorphous.

Moreover, a variation in the solvent content and solvent temperature causes drastic variations in the rheologic properties of the solution. This phenomenon creates many opportunities, including gel 3D printing. One example of exploiting this phenomenon is that of the work conducted by Lei Li et al. [51]. In the article, the team successfully 3D printed 5 g of cellulose from a 100 ml NMMO-Water (50% w/w) solution at 70 °C, in which, following printing, the gel solidified, holding the printed shape, to have NMMO later extracted by submerged in Milli-Q water bath (to avoid contaminating the sample with bacteria for its use as a scaffold) and further water extracting through freeze-drying. The

final product, shown in Figure 13, was reported to have a Young's modulus of 160 MPa and a fracture toughness of 2.6 MPa at an elongation of 1.63%.
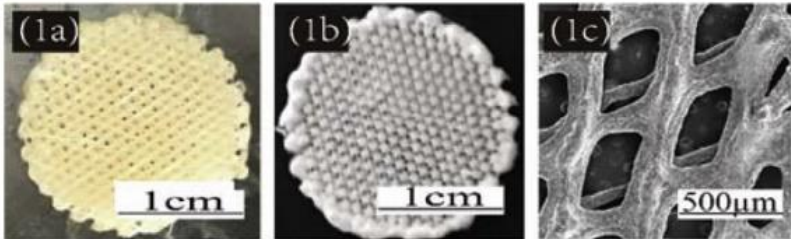
Figure 13: 3D Printed mixture of Cellulose + NMMO/50% water gel at 70°C. Pre freeze-drying product (1a), post freeze-drying product (1b) and SEM micrograph of the post freeze-drying product (1c). Credit: Lei Li et al. School of Materials Science and Engineering, University of Shanghai for Science and Technology

In regard to the ability to convert NMMO-dissolved cellulose to individualized nanocellulose capable of working as a reinforcing filler in a PLA matrix, Kowalczyk et al. [52] successfully produced a PLA composite with 2 wt% of nanocellulose obtained by electrospinning a NMMO solution following the procedure described by Piotr Kulpinski [53]. To mix the cellulose with PLA, Kowalczyk et al. prepared a 15 wt% PLA dichloromethane solution and subsequently added the electrospun cellulose nanofibers to the solution. The dichloromethane solvent was extracted in a furnace set to 100 °C during 12h and the solid was later processed in a mixer at 170 °C under a nitrogen atmosphere, to later be extruded to normalized test samples. The same procedure with normal-sized cellulose fibers was followed in order to compare results.

The tensile testing resulted in a composite with a yield strength of 50.7 MPa, a Young's modulus of 2 GPa and an elongation at fracture of 12 %, values only slightly better to that of unfilled PLA (48.2 MPa, 1.8 GPa and 21 %, respectively). Moreover, the DSC test profile did not seem to indicate a change in the glass transition, crystallization or fusion temperature of the PLA, which suggest that the presence of cellulose did not affect the structural properties of PLA. The FESEM micrograph of the obtained composite is shown in Figure 14. In regard to the size of nanocellulose fibers obtained by the

electrospinning method, micrographies indicate a diameter range of 200-300 nm, illustrated in Figure 15.

Figure 14: FESEM spectroscopy of the fracture surface of a PLA - 2% nanocellulose obtained by NMMO-solution electrospinning. Credit: M. Kowalczyk et al. Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences
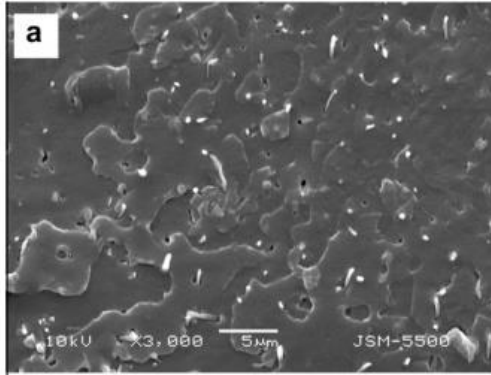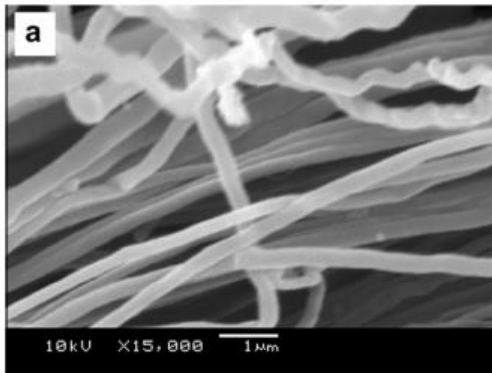

Figure 15: FESEM spectroscopy of electrospun cellulose fibers obtained in an NMMO solution system. Credit: M. Kowalczyk et al. Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences

6.2.   INTERACTION OF CELLULOSE AND ITS DERIVATIVES IN A PLA MATRIX

In the study of Kowalczyk et al. [52], a small addition of 2 wt% CNC to the bulk of the PLA matrix did indeed produce interesting results to its mechanical properties. Nonetheless, the study still leaves many questions unanswered. The most obvious is whether it is possible to create a composite with a larger nanocellulose fraction than just 2 wt%. Moreover, as he seems to suggest in the studies, the mixture of nanocellulose and PLA was not done through a common solvent, but rather through a likely suspension of nanocellulose in dichloromethane. Therefore, the study does not point to the feasibility of dissolving larger quantities of electrospun NMMO-nanocellulose in their solvent of choice, dichloromethane.

Furthermore, as studied in [54], an intimate electrostatic -or even chemical- interaction between the surface of a filler and a matrix in a composite, such as the interaction of a Mg filler in a PLA matrix in the case studied by [54], is not only critical for a correct dispersion of the particles in a matrix and the conservation of its thermodynamic properties [55], but also essential in improving the mechanical properties of the resulting composite, since a strong interaction between filler and matrix allows for a better mechanical load transmission across the bulk of the composite [56].

Nonetheless, in the case of the NMMO nanocellulose + PLA composite of Kowalczyk et al., this intimate interaction does not seem to be evident. While it is true that it has been demonstrated that regenerated cellulose from NMMO solutions possess a highly fibrous microfibril surface morphology [57], which can be beneficial in increasing the contact area between fiber and filler in a composite material, this might not necessarily result in a better interaction with matrices such as PLA. For instance, if we look at the fracture surface of the sample tested by Kowalczyk et al. illustrated in Figure 14, it is evident that in many regions where cellulose fibers are visible, an intimate welding between the fibers and the PLA matrix is not visibly strong.

On the other hand, in a similar experiment where a mixture of PLA and 2 wt% TEMPO-mediated oxidized Bacterial-CMC was obtained by dissolving both PLA and CMC in dichloromethane [58], the surface morphology of a fracture sample of such composite, illustrated in Figure 16, shows a much more intimate bonding between the visible CNFs

and the PLA matrix, as characterized by the absence of gaps between the fiber and the matrix, or a difficulty in distinguishing between the two, which suggests a covalent bonding between matrix and filler, which is further supported by points in which it seems that fibers are "dragging" the surrounding matrix in the direction of traction.
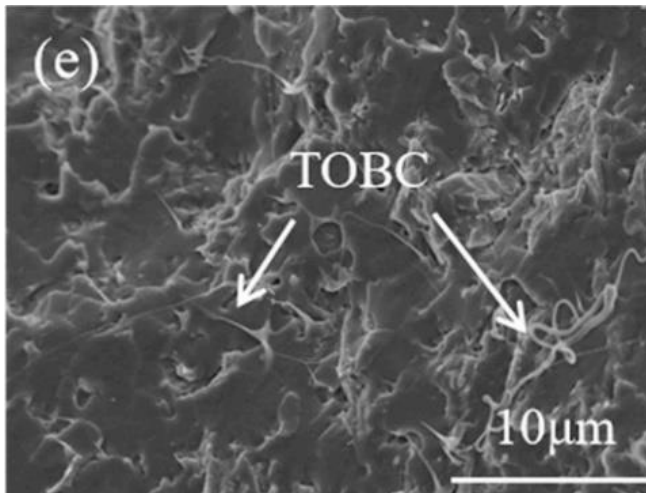

Figure 16: FESEM spectroscopy of the fraction surface of a PLA – 2 wt% TOBC composite obtained in a DCM solution system and extrusion. Credit: Luyao Li et al. a State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Material Science and Engineering, Donghua University

Therefore, it is reasonable to affirm that the surface modification of cellulose with TEMPO-mediated oxidation by substituting hydroxyl groups for carboxymethyl groups does make for a better prospect at strengthening the ability of cellulose of not only being more readily dissolvable in solvents but also forming stronger bonds with other materials such as PLA.

As such, several other studies have proved that celluloses or cellulosic materials whose interfaces have been modified by carboxymethylation have shown better adhesion to the matrix, no tendency to agglomeration and better overall improvements in composite mechanical properties [59], [60]. Thus, it makes more sense to further study the interactions of CMC with PLA matrices and measure the degree to which such surfaces modifications strengthen the surface bonding between PLA matrix and CNF filler.

The correct measurement of surface bonding forces between polymer and filler in a composite setting is paramount in determining the ultimate mechanical properties of a composite material. Bonding forces that are too weak or too strong can produce adverse effects, and it is often desired to control these forces precisely to achieve optimal properties. For instance, in carbon-carbon composites for high-temperature applications [61], a high chemical bonding between resin and carbon fiber restrains matrix shrinkage during the matrix carbonization and reduces the composite flexural strength. The increased chemical bonding provides no fiber debonding mechanism during elongation, which results in a catastrophic propagation of cracks in the matrix, resulting in a brittle composite. When this chemical bonding strength is reduced down to an optimal range, the cracks that are produced when fibers reach their ultimate tensile strength can be deflected on the fiber-matrix interface thus increasing the composite fracture toughness. However, making such a study is not straightforward.

While there is ample literature to macroscopically measure and analyze the surface interaction of millimeter or even micrometer-sized fibers in a polymer matrix [62], such measurements at the nanoscale require different approaches. While studying the effects of surface modification of vapor-grown carbon nanofibers in improving the fiber adhesion to a Polypropylene (PP) matrix, Lafdi et al. noted that an increase in the fibers surface functionalization treatment time produced an increase in the PP-carbon nanofiber composite tensile and elastic strength [63]. To analyze the degree of functionalization, X-

Ray photoelectron spectroscopy (XPS) of functionalized samples and Chemical derivatization XPS, a technique that consists in selectively derivatizing functional groups of interest, was used to characterize functional groups whose chemical shifts are below the energy resolution attainable by XPS. A correlation between the XPS results and the bulk mechanical properties was established. Moreover, fracture surface SEM micrographs revealed a clear distinction between the non-derivatized and derivatized carbon nanofibers in terms of adhesion to the PP matrix, in which derivatized fibers show a clear increase in contact angle with the PP matrix, as depicted in Figure 17.
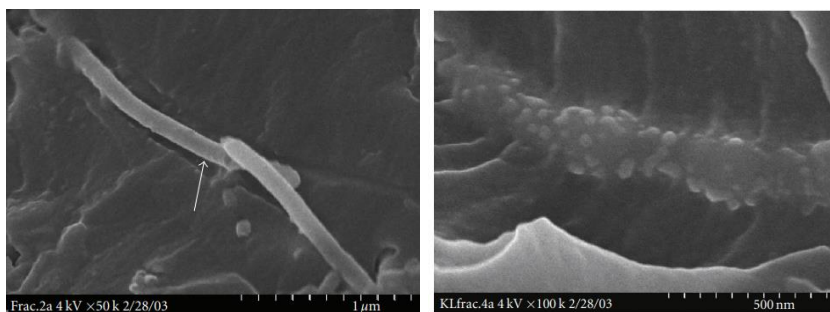
Figure 17: Non-derivatized carbon nanofibers (left) and Derivatized carbon nanofibers (right) in a PP surface fracture matrix. Credit: Khalid Lafdi, William Fox, Matthew Matzek, and Emel Yildiz, University of Dayton

Another technique that has proven to show great potential for characterizing polymer composites and measure its various properties, even at the nanoscale, is the Atomic Force Microscopy (AFM), whose versatility in scanning modes and ability to indent samples, functionalize tips and drag samples [64] enables the measurement of intricate properties between matrix and nanofiller in polymer composites.

As such, Effah et Al has studied the applications of AFM to characterize the interfacial adhesion of wood fibers in different polymeric matrices [65]. By functionalizing the tip with targeted groups and measuring the pullout force between the AFM tip and the matrix surface, it was concluded that through mathematical models that assume different interactive natures, it is possible to quantify the surface binding force between the functional group and the matrix. It is also possible to quantify the degree of functionalization through AFM by measuring characteristic interaction forces.

AFM also proved as a useful technique to quantify nanofiber mechanical properties at the nano scale. Early nano-indentation techniques allowed researchers to estimate the mechanical properties of materials at the nanoscale. Nonetheless, these techniques require several assumptions in material behavior that often don't correlate with macro observations [66]. In contrast, AFM proves difficult to control the exact position of fibers by its own.

However, recent techniques combining AFM + SEM have proved successful in real time measuring precise fiber properties. One such example is the work of Hang et al., which used a combination of vacuum epoxy glue at the tip of the AFM and at the base of the sample holder to measure in-situ the mechanical deflection produced by the tip pulling force and thus drawing a real-time stress-strain curve for electrospun PVA, nylon-6 and mineralized collagen (MCF) nanofibers [67], as depicted in Figure 18.
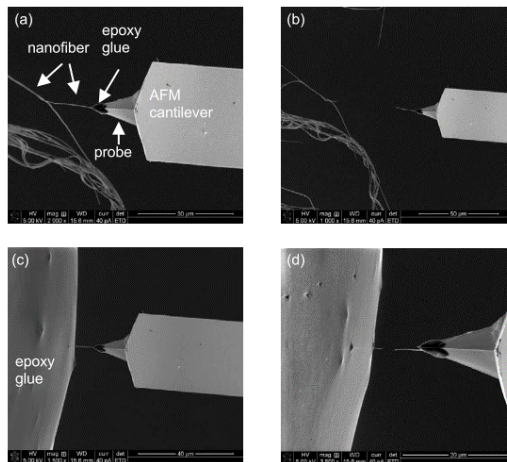
Figure 18: SEM micrograph showing a tensile test of electrospun nanofibers (PVA) using in situ AFM–SEM. Credit: Fei Hang et al. Department of Materials, School of Engineering and Materials Science, Queen Mary. University of London.

With this technique, a stress-strain curve was able to be drawn (Figure 19) and a larger tensile strength and elastic modulus of the PVA fiber as compared to the bulk material was observed. Therefore, the AFM technique could also be used to both characterize the surface interaction of a PLA + Nanocellulose composite and be used to compare the results that different degrees of cellulose derivatization would have in both altering the matrix surface interaction and the mechanical properties of the nanocellulose nanofibrils themselves.
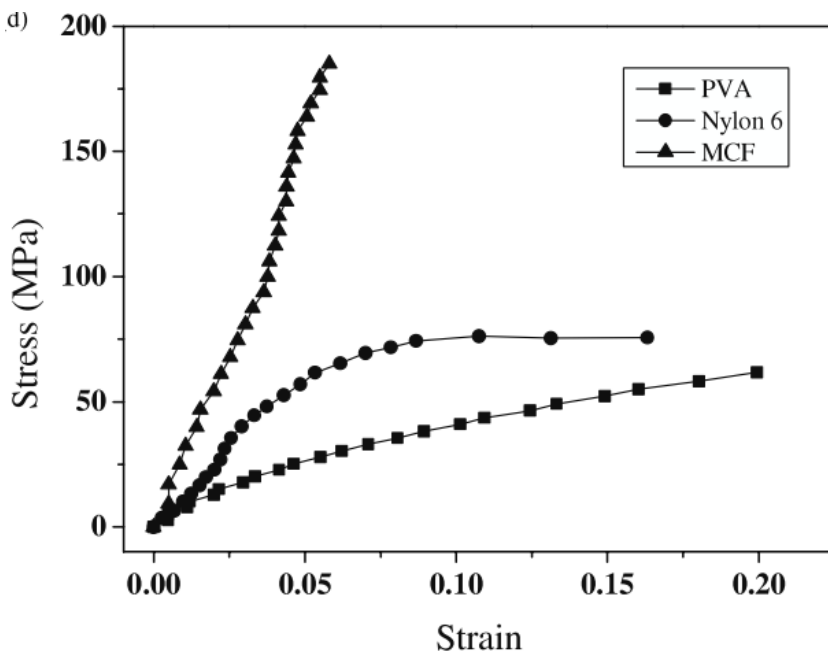
Figure 19: Stress-strain behavior of PVA, nylon-6 and MCF nanofibers by AFM-SEM nanofiber tensile testing. Credit: Fei Hang et al. Department of Materials, School of Engineering and Materials Science, Queen Mary University of London

7. TECHNO-ECONOMIC ANALYSIS OF A PLA - NANOCELLULOSE COMPOSITE

The main ways to chemically obtain individualized nanocellulose fibers are the derivative and non-derivative routes, being the most prominent TEMPO-mediated oxidation [68] and NMMO dissolution [52], respectively, for each route. For its use as a PLA-matrix composite, a good interaction between the nanofiber particles and the matrix is very important, and the technique that seems to give the best surface interaction with PLA is the TEMPO-oxidized cellulose, as it alters the chemical behavior of its surface, making it more compatible to the hydrophobic nature of PLA.

However, from an economic standpoint, in regards to transforming laboratory-grade solutions to real-world applications, it is equally important to analyze the techno-economic aspects of a desired technique, since more often than not, for factors outside of the scope of an optimal technological solution, such as cost or market-fitness, many patented processes end up being uneconomical [69]. Therefore, to produce a PLA – Nanocellulose composite, we will consider a production process using the TEMPO-mediated method for obtaining nanocellulose and list industry standardized techniques to analyze the costs of obtaining a PLA – Nanocellulose composite.

7.1. TECHNICAL DESIGN OF A PLA – NANOCELLULOSE COMPOSITE FROM TEMPO–MEDIATED OXIDIZED INDIVIDUALIZED CNFS

For producing a PLA – TEMPO-mediated oxidized nanocellulose composite, we will propose a modified technique of that employed by Luyao Li et al. [58]. The team's technique consists in producing a Pickering emulsion of PLA dissolved in Dichloromethane and TEMPO-mediated oxidized Bacterial Cellulose (BC) dispersed in water, which is then mixed in a sonicator to allow the nanocellulose to be transferred to the PLA particles. Since the team uses BC as a cellulose source, which is characterized

by a fibrous, micrometer-sized morphology, our modification will mainly address previous preparations required to employ Soy Husks as a cellulose source.

7.1.1. Preparation of TEMPO-mediated oxidized CNFs from Soy Husks

Previous attempts at the Department of Materials Science and Physical Chemistry have been made at producing nanocellulose crystals [5]. Those attempts have focused primarily on the widely known acid hydrolysis derivative method. Regardless of their success at individualizing nanocellulose, it is important to know that to convert Soy Husks to Cellulose, a standard bleaching process widely adopted at the paper industry to remove from Soy Husks other products such as lignin or hemicellulose can be followed [70]. The resulting product is a somewhat sandy cellulosic product with agglomerated particles.

To prepare the bleached cellulose from Soy Husks for TEMPO-mediated oxidation, the procedure followed by T. Saito et al. is suggested [68]. As it was reported, the TEMPO-mediated oxidation of 1 g of cellulose with a yield of 90% requires the reagents listed on Table 1. According to the author, the reaction time and yield are heavily dependent on pH. The role of NaOH and HCl is thus to control the pH of the solution during reaction. As such, an optimal pH of 10 was determined to yield the fastest reaction time at room temperature, 130 minutes and at 500 rpm stirring of the reagent solution.

The reaction followed by T. Saito et al. is carried out as follows. A 100 mL water solution with 1 g of dispersed cellulose suspension is prepared via stirring. Additionally, a 12 wt% NaClO solution is prepared and adjusted to pH 10 with 0.1 M HCl. Reagent quantities required for pH adjustment are not specified. To activate the TEMPO-mediated oxidation reaction, an equivalent volume containing 0,2 g of NaClO is extracted from the previous solution and added to the water-cellulose suspension along with a desired quantity of 0,5 M NaOH to keep the pH at 10 at all times. As the oxidation progresses, NaClO will be consumed, and the pH is kept at 10 by continuously adding 0,5 M NaOH as required. The reaction is expected to be completed until no more NaOH is consumed.

Table 1: Reagents required for TEMPO-mediated oxidation of 1 g bleached cellulose. Credit: Tsuguyuki Saito et al. Department of Biomaterials Sciences, Graduate School of Agricultural and Life Sciences, The University of Tokyo.

Reagent	Quantity	Role
Deionized water	100 mL	Reaction solvent
TEMPO	0,016 g	Catalytic mediator
Sodium bromide	0,1 g	Oxidation agent
Sodium hypochloride4	0,1 g	Oxidation agent
Sodium Hydroxide	NA	pH control
Hydrochloric acid	NA	pH control

Under the conditions of pH 10 and 500 rpm stirring at room temperature, the author reports a total reaction time of 130 minutes. Upon completing the reaction, 90% recovery rate is reported. The final product is then washed with water and stored at 4 ºC.

For the purposes of moving to the next step of the composite production, we suggest the final product to be washed, centrifuged and stored at 4 ºC.

7.1.2. Preparation of PLA/Nanocellulose gel

The main differences of the procedure by T. Saito et Al and the procedure proposed on this Work starts here. To prepare the composite mix, the author first dissolves 10 wt% PLA in CH_2Cl_2 which is stirred at room temperature for 4 h to ensure entanglement of PLA molecules. However, different experiments involving a production of PLA solution report varying dissolution times [71]–[73]. Thus, it can be inferred that the optimum time for dissolving PLA might be shorter than 4 h.

Another point of divergence with the procedure proposed T. Saito et Al is the mixing step of the TEMPO-oxidized cellulose with the PLA – CH_2Cl_2 solution. His procedure calls for mixing the two components through a Pickering Emulsion, depicted in Figure 20. Pickering Emulsions are particularly useful for reducing particle coalescence in immiscible solvents [74], and in the case of a PLA – nanocellulose setting, homogenous dispersion of nanocellulose fibers is achieved at the surface of PLA microspheres, as shown in Figure 21. However, several studies achieved effective dispersion of cellulose nanocrystals in CH_2Cl_2 through simple mechanical agitation [75]–[77]. Thus, there is reason to believe that TEMPO-oxidized cellulose shows a low degree of coalescence in

CH_2Cl_2, and therefore a Pickering Emulsion need not be pursued, as simplifying the solvent composition can help increase the recoverability of CH_2Cl_2.

Once a homogenous mixture is attained, obtaining viscosities of a gel can be attained by simple solvent extraction. According to the author, the emulsion of BC and PLA was placed in a fume hood for 24 h to allow for CH_2Cl_2 evaporation and then was dried in an oven at 60 ºC for 24 h. The selection of the optimum solvent removal procedure will depend on the final desired applications. For instance, methods such as freeze-drying, which is based on achieving a solid to gas transition of the solvent by using low temperatures and pressures, can be considered as a more efficient alternative both for eliminating the solvent and producing porous structures which can then be employed in high-surface area application or compacted for extrusion [78], [79].
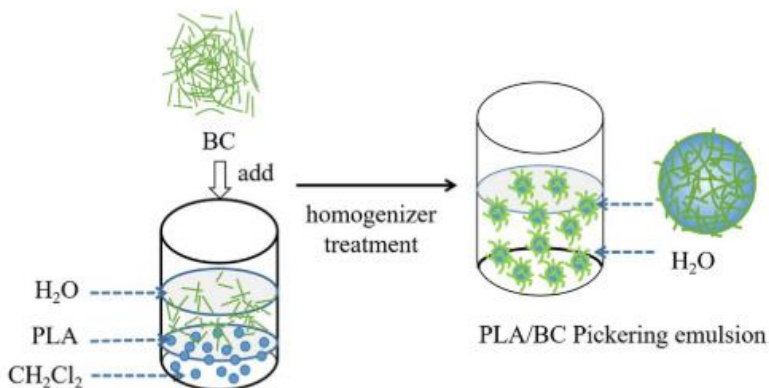
Figure 20: Schematization of a Pickering Emulsion of PLA - BC in a water - dichloromethane solution. Credit: Luyao Li et al. College of Material Science and Engineering, Donghua University, Shanghai
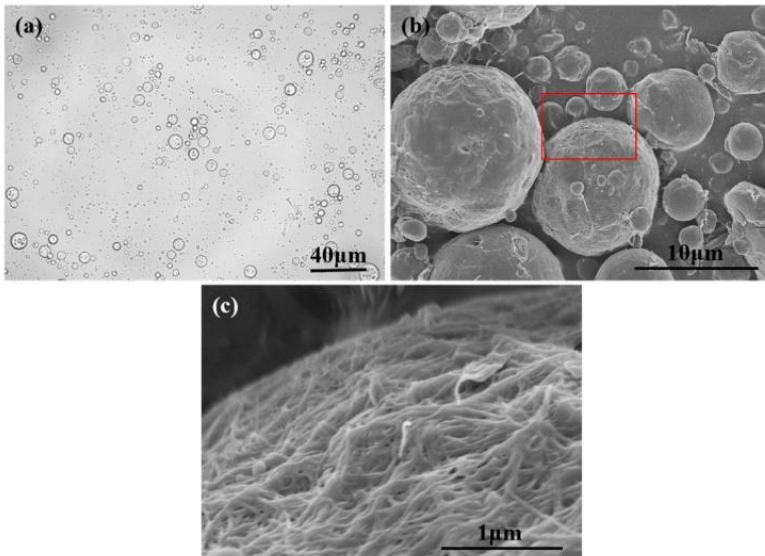
Figure 21: Microscopic (a) and SEM (b, c) images of the nanocellulose-covered PLA microspheres formed as a result of the Pickering Emulsion process. Credit: Luyao Li et al. College of Material Science and Engineering, Donghua University, Shanghai

7.2. ECONOMIC ANALYSIS OF PRODUCING A PLA – NANOCELLULOSE COMPOSITE

In order to carry out a detailed economic plan, the compounds used for PLA synthesis must be taken into account and whether this procedure is carried out in situ or by different suppliers. However, since such a composite is not currently found in the market in an industrial scale, the results studied in the bibliography studied cannot be taken as conclusive. The economic costs associated with producing Nanocellulose Crystals is contemplated based on the more commonly known acid hydrolysis method and is discussed on the following section.

7.2.1. Economic costs of Nanocellulose production via acid hydrolysis

As a relatively novel material, Nanocellulose has yet to find massive market adoption, thus, relatively little literature exists around its production methods on an industrial scale, and of those, many are industrial secrets. However, some literature on the most common

procedure for producing nanocellulose crystals, the non-derivatizing acid hydrolysis technique, does exist. On their study, Abbati de Assis et al. produced an extensive analysis on the prospects of the market for nanocellulose, the current techniques in place, and present value evaluation of different production scenarios [80].

Currently, the market for Nanocellulose sits at a global value of USD 65 Million and produced 13870 tons of material with main applications as a viscosity modifier and in the paper industry. The author reports that it has been estimated that the industry will grow by a compounded annual growth rate of 30% in the years ahead, although some uncertainty exists due to potential new applications expected to emerge.

One of the main factors that affects the economic costs of producing nanocellulose is the energy consumption required by the processes followed. As it has been previously discussed, individualization of cellulose nanofibers is produced mainly through mechanical agitation, thus, the weaker the bonds between nanofibers, the less energy the process consumes. It has been reported that a reduction from more than 10,000 kWh/t to just 500 kWh/t of energy consumption can be achieved by carboxymethylation of kraft pulps, as produced by TEMPO-mediated oxidation [81]. However, as Abbati de Assis et al. points out, a more accurate analysis of acid hydrolysis carbon nanocrystals can be better studied as proprietary processes such as the AVAP Technology from American Process Inc. and the R3 technology from Blue Goose Refineries are already in place industrially.

The production design of a CNC manufacturing plant proposed by Abbati de Assis et al. is depicted in Figure 22. The process is characterized by a bare ground project independent from kraft producers and runs on Dissolving pulp (> 90% cellulose content) at a production capacity of 50 t / day continuously, with acid recovery. Other scenarios contemplated a plant without acid recovery, which would require acid neutralization before disposal, or a plant produced in co-location but independently from a kraft producer.

In Figure 23, Figure 24 and Table 2, a depiction of the Capital Investments, Return on Investment (ROI) and Payback period for the different scenarios studied is illustrated. With the study, the author concludes that the major cost drivers of profitability are associated with capital investment and feedstock costs on all scenarios, being the co-location, non-acid-recovery process the one producing the lowest minimum product

selling price (MPSP) of CNC, rated at 4,829 USD/t without drying the final CNC product and 6,522 USD/t with CNC drying. For comparison, in 2017, export prices of PLA in the United States have ranged from 2,040 USD/t to 1860 USD/t [82], whereas one of the most commonly used fillers in PLA, that is, Talc [83], trades at around 230 USD/t [84]. Therefore, although CNC prices are considerably higher in comparison to fillers such as Talc**,** it is still worth exploring the economies of TEMPO-oxidized cellulose nanofibers from food waste products such as Soy Husks as the feedstock costs and energy savings could potentially lower the final MPSP of Nanocellulose, and coupled with its benefits in strengthening PLA matrices, could make for very economical applications.

Figure 22: Block Diagram for CNC manufacturing starting as a bare ground project. Credit: Camilla Abbati de Assis , Department of Forest Biomaterials, North Carolina State University, Raleigh, USA.

Figure 23: Capital investment requirements estimated to create a 50 t/day CNC production plant.
Credit: Camilla Abbati de Assis , Department of Forest Biomaterials, North Carolina State
University, Raleigh, USA
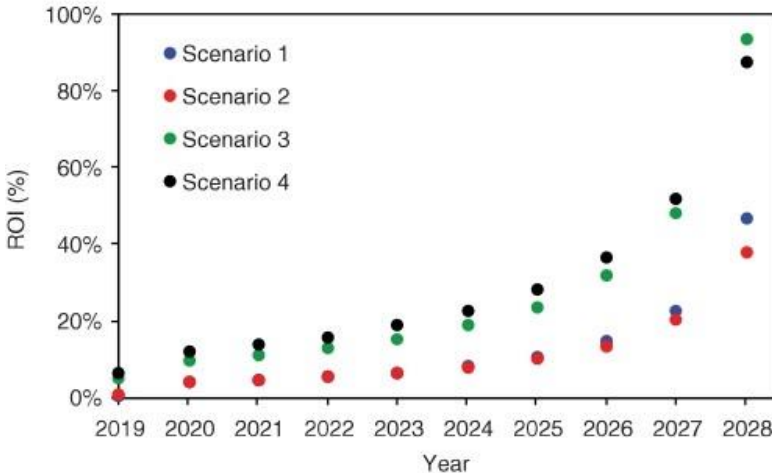

Figure 24: ROI of the different scenerios studied in the techno-economical analyisis of
industrial Cellulose Nanocrystals. Credit: Camilla Abbati de Assis , Department of Forest
Biomaterials, North Carolina State University, Raleigh, USA

Table 2: Payback period for scenarios 1 to 4 in the techno-economical analysis of industrial Cellulose Nanocrystals production. Credit: Camilla Abbati de Assis , Department of Forest Biomaterials, North Carolina State University, Raleigh, NC, USA

	Base-case (Scenario 1)	Scenario 2	Scenario 3	Scenario 4
Payback period (years)[a]	10.2	10.4	8.1	7.6

[a]considering CNC selling price = USD 4829/t of CNC (dry equivalent).

7.3. NEXT STEPS IN THE PRODUCTION OF PLA – NANOCELLULOSE COMPOSITES

As discussed on this thesis, ample evidence points to the possibility of creating a PLA – Nanocellulose composite material with properties that could amplify the field of applications for PLA and enforce its application in more technical fields such as that of biomedicine. However, many questions are still left unanswered and those who proceed this research effort should aim at addressing those as we move towards creating a mass-production grade PLA – Nanocellulose composite.

Of those questions, the most relevant are the ones concerning the surface interaction of PLA and Nanocellulose, in particular, the quantitative effect of nanofiber surface functionalization in modulating the PLA – fiber surface bonding. XPS and a combination of AFM + FESEM can be used as methods for both characterizing the type and quantity of functional groups present as a function of TEMPO-oxidation reaction time. Moreover, a traditional stress-strain test can be performed to identify the bulk impact of the degree of functionalization. Another question that arises from the study is the degree to which different quantities of nanocellulose can be mixed with PLA and to what extent does a higher quantity impact the composite mechanical properties, since of all the studies referenced, none attained PLA to cellulose ratios of more than 20 wt%.

Therefore, to answer those questions, an experimental table, detailed in Tables 3 to 10 is proposed. Each different sample represent a unique experimental variable and together they

should provide a clearer picture of the interaction between PLA and Nanocellulose. For instance, samples C1 and C2 on

Table 5 compare the effect of time on cellulose delignification, sample C3 on

Table 6 compare the effect of temperature and time on the final bleaching of cellulose, sample C1-A and C1-B on table Table 8 compare the effect on oxidizer quantity on reaction time and final cellulose properties, C2-A and C2-B on Table 8 compare the effect of temperature on the reaction time and final cellulose properties. Samples C1-A and C2-A on Table 9 compare the effect of mechanical individualization time of final cellulose properties and finally Table 10 describes the process with which CNFs can be individualized.

Another interesting variable that should be addressed by future researchers is the degree to which longer-sized CNFs affect the composite properties and what processes can be followed to control resulting nanocellulose fiber lengths, as it has been proven multiple times that in nanofiber-filled composites, fiber geometry, in particular, fiber length, shows a direct correlation in the bulk mechanical properties [85]–[87].

Before continuing to each step in the experimental setting, the researcher should put strong emphasis on collecting small samples for morphological observation under FESEM and for thermal properties analysis under DSC since those reflect some of the most important features for using cellulose as a filler in a PLA matrix composite, namely particle size and thermal degradability in the face of processes such as extrusion or injection molding.

Table 3: Starting cellulose source preparation.

Characteristics of base product: Cellulose from Soy Hulls		
Milling with Vibrating Disk Mill, Temperature controlled*	Sieved with 0,5 mm mesh	Quantity 60 g
*Temperature control during milling required to minimize polymer softening		

Table 4: Summary of pre-TEMPO cellulose samples and summary of cellulose delignification and bleaching variables to be modified for each sample.

Core Samples	Weight (g)	Bleaching Technique	Delignification Time
Control	5	none	none
C1	25	H_2O_2	2 h
C2	25	H_2O_2	24 h
C3	5	H_2O_2	2 h

Table 5: Description and variables of the delignification process for each cellulose sample.

Delignification						
Sample	Reactives	Quantity	Concentration	Temperature	Time	Procedure
C1	NaOH	250 mL	15 wt%	353 K	2 h	Agitation at 400 rpm during procedure, followed by dilution in distilled water, decanting and extraction with ethanol, drying in desiccator.
	Cellulose	25 g	-			
C2	NaOH	200 mL	15 wt%	353 K	24 h	
	Cellulose	25 g	-			
C3	NaOH	250 mL	15 wt%	353 K	2 h	
	Cellulose	5 g	-			

Table 6: Description and variables of the bleaching process for each cellulose sample.

Bleaching						
Sample	Reactives	Quantity	Concentration	Temperature	Time	Procedure
C1	H₂O₂	70 mL	30 wt%	363 K	40 min	Bleach under agitation at 400 rpm. After bleaching, wash with distilled water, decant until mother liquor is pH neutral, then wash with ethanol and dry in oven.
	Cellulose	25 g	-			
C2	H₂O₂	70 mL	30 wt%	363 K	40 min	
	Cellulose	25 g	-			
C3	H₂O₂	15 mL	30 wt%	ambient	24 h	
	Cellulose	6 g	-			

Table 7: Summary of solution compositions to be used during the TEMPO-mediated oxidation of cellulose.

Solution types for TEMPO-mediated oxidation		
Standard proportions per 1g cellulose		
Base Solution	Reagent	Quantity
	Water	100 mL
	TEMPO	0.016 g
	NaBr	0.1 g
Oxidant Solution	12 wt% Sodium Hypochlorite Solution adjusted to pH 10 with 0.1 M HCl	2.5 and 5 mmol
pH Control	0,1 M HCl	as required
	0,5 M NaOH	as required

Table 8: Description of the TEMPO-mediated oxidation process and variables for each cellulose sample.

Sample	Reactives	Quantity	Temperature	Time	Procedure
TEMPO - mediated oxidation					
C1-A	Base solution	100 mL/g cellulose	amb	as required	Prepare the base solution and disperse the desired quantity of cellulose therein. Separately, prepare the oxidant solution and the devices for pH control. Keep pH at 10 by adding NaOH, as the reaction consumes OH⁻. Reaction will be finished until no more NaOH is consumed. Once finished, wash and filter with water and store at freezer in water solution.
C1-A	Cellulose	Split C1 yield in equal parts			
C1-A	Oxidant solution	2.5 mmol			
C1-B	Base solution	100 mL/g cellulose	amb	as required	
C1-B	Cellulose	Split C1 yield in equal parts			
C1-B	Oxidant solution	5 mmol			
C2-A	Base solution	100 mL/g cellulose	amb	as required	
C2-A	Cellulose	Split C2 yield in equal parts			
C2-A	Oxidant solution	2.5 mmol			
C2-B	Base solution	100 mL/g cellulose	323 K	as required	
C2-B	Cellulose	Split C2 yield in equal parts			
C2-B	Oxidant solution	2.5 mmol			

Table 9: Description of the individualization process and variables of cellulose nanofibers for each TEMPO-mediated oxidized cellulose sample.

Nanocellulose Individualization			
Sample	Temperature	Time	Procedure
C1-A	amb	30 min	Prepare a 5g/100 mL TEMPO-mediated oxidized cellulose dichloromethane suspension and use ultrasonication at 600W for mechanically individualize particles
C1-B	amb	30 min	
C2-A	amb	60 min	
C2-B	amb	30 min	

Table 10: Description of the preparation of a PLA - Nanocellulose composite for each cellulose sample.

PLA Composite preparation	
Sample	Procedure
C1-A	Prepare a 20g/100 mL PLA - dichloromethane solution and mix the solution with the corresponding nanocellulose solutions, then ultrasonicate at 600W for 3 minutes. Afterwards, pour solution in a flat panel and over-dry at 320 K.
C1-B	
C2-A	
C2-B	

8.   CONCLUSIONS

The goal of this thesis was to obtain a PLA + Nanocellulose composite. However, due to the unprecedented circumstances as a result of the COVID-19 outbreak, a bibliographic collection of techniques and potential routes for producing the composite was studied and a technique for obtaining the composite was proposed.

Different processes for obtaining individualized derivative CNFs, with the required surface properties for their coalescence with the PLA matrix, were discussed. Of those cellulose-individualization processes, TEMPO-mediated oxidation of cellulose has proven to be the most desirable for its use in PLA composites for several reasons:

- It adds functional groups at the surface of cellulose nanocrystals that in one hand, reduces the hydrogen bond interaction between other crystals and drastically reduces the energy required for nanofiber individualization, and on the other hand, considerably improves the adhesion of cellulose fibers to a PLA matrix.
- It provides a cost-effective and single-step process for producing nanofibers which can then be stored as a solid product and later be re-individualized in solution by low-energy mechanical trituration.
- It requires cheap reagents which are easily available.

Prominent production designs were reviewed for carrying out TEMPO-mediated oxidation, and simplifications such as single-solvent mixing and reduced dissolution time were proposed based on additional literature found on the subject-matter.

Finally, an economic analysis of the prospect of producing PLA – Nanocellulose composites was briefly discussed, in which it was concluded that the TEMPO-mediated oxidation process has the potential to be economic feasible and future experimental settings were proposed to further validate the behavior between PLA and Nanocellulose in a composite setting.

9.   REFERENCES AND NOTES

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