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Development and characterization of thermoplastic polymeric materials, reinforced by inclusion of cellulose nanoparticles

Desarrollo y caracterización de materiales poliméricos termoplásticos reforzados mediante la inclusión de nanopartículas de celulosa

Desenvolvemento e caracterización de materiais poliméricos termoplásticos reforzados mediante a inclusión de nanopartículas de celulosa

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July 2020

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CERTIFY:

That the work described in the present report, titled "**Development and characterization of thermoplastic polymeric materials, reinforced by inclusion of cellulose**", was carried out under their guidance by Ms. Eva María del Campo Ortiz for CETIM Company by a bibliographic research. Once concluded, they authorize its presentation as a Final Degree Dissertation Report.

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Abbreviations

A: Poly (adipate diethylene)	PEO: Poly (ethylene oxide)
ANP: Amorphous nanoparticles	PET: Polyethylene terephthalate
ATRP: Atom transfer radical polymerization	PET: Polyethylene terephthalate
BiB: Bromoisobutryl bromide	PGA: Polyglycolide
BNC: Bacterial nanocellulose	PGA: Polyglycolide
CNC: Cellulose Nanocrystals	PHA: Poly (hydroxyalkanoate)
CNF: Cellulose Nanofibrils	PHB: Poly (hydroxybutyrate)
CNP: Crystalline nanoparticles	PHB: Polyhydroxy butyrate
CW: Cellulose whiskers PHBV:	PLA: Polylactic acid
DMF: Dimethylformaldehyde	PMMA: Polymethyl metacrylate
DS _{surface} : Degree of Substitution on the Surface	Poly (3-hydroxybutyrate-co-3-hydroxyvalerate)
EVA: Polyethylene-co-vinyl acetate	PP: Polypropylene
FTIC: Fluorescein isothiocyanate	PPC: Polypropylene carbonate
GTMAC: Glycidyltrimethylammonium chloride	PS: Polystyrene
HDPE: High-Density Polyethylene	PS: Polystyrene
LBL: Layer by layer	PTT: Poly (trimethylene terephthalate)
LDPE: Low density polyethylene	PUR: Polyurethane
MFC: Micro fibrillated cellulose	PVA: Poly (vinyl alcohol)
OTR: Oxygen transmission rate	PVC: Polyvinyl chloride
PA: Polyamide	ROP: Ring opening polymerization
PA6: Polyamide	SET-LP: single-electron transfer living radical polymerization
PCL: Polycaprolactone	S _N 2: Nucleophilic substitution
PE: Polyethylene	TB: Tributyrin
PEF: Poly (ethylene 2,5-furandicarboxylate)	TDI: tolylene-2,4-diisocyanate
PEG: Polyethylene glycol	TEMPO: 2,2,6,6-Tetramethylpiperidine-1-oxyl
	WVTR: Water vapor transfer rate

Abstract

The aim of my project is the planning of development and characterization of new composites consisting on polymers with improved mechanical, thermal and barrier properties, obtained using mainly nanocellulose as reinforcements. It is focused on the study and chemical modification of nanocellulose surface, to improve the compatibility with polymers. In turn, alternative modified polymers will be studied. The objective is to achieve composites with appropriate characteristics, enhancing the relation between matrix and dispersed phase. When both parts, polymers and modified nanocellulose are prepared, the composites will be created. In addition, the percentages of each part will vary to improve polymer properties. The final composites will have applications such as food packing, caps, automobile parts, reusable bags, trays and containers, toys, houseware and building insulation materials among others.

This TFG focuses on the bibliographic study of the materials, strategies and techniques to be developed. It should be noted that this TFG project results from the modification of the initially proposed, which included mostly experimental work at CETIM company. The development of the normal path of this project was interrupted by the exceptional situation of COVID-19. After the publication of *Real Decreto 463/2020*, on March 14th, which stated the state of alarm due to the health crisis management caused by COVID-19, I had to perform my final project at my home address, converting the project in this bibliographic research.

Resumen

El objetivo de mi TFG es la planificación del desarrollo y caracterización de nuevos materiales que consisten en polímeros con propiedades mecánicas, térmicas y de barrera mejoradas, utilizando principalmente nanocelulosa como refuerzos. Se centra en el estudio y la modificación química de la superficie de la nanocelulosa, para mejorar la compatibilidad con los polímeros. A su vez, se estudiarán modificaciones de los polímeros. El objetivo es lograr materiales con características apropiadas, mejorando la relación entre la matriz y la fase dispersa. Cuando esta compatibilidad se alcance para ambas partes, polímeros y nanocelulosa, se crearán los “composites”. Además, los porcentajes de cada parte variarán para mejorar las propiedades del polímero. Los materiales finales tendrán aplicaciones tales como el envasado de alimentos, tapas, piezas de automóviles, bolsas reutilizables, bandejas y contenedores, juguetes, artículos para el hogar y materiales de construcción, entre otros.

Este TFG se centra en el estudio bibliográfico de los materiales, estrategias y técnicas a desarrollar. Cabe señalar que este TFG es el resultado de la modificación de la propuesta inicial que incluía principalmente trabajos experimentales en la empresa CETIM. El desarrollo del proyecto fue interrumpido por la situación excepcional de COVID-19. Después de la publicación del *Real Decreto 463/2020*, el 14 de marzo, que declaró el estado de alarma debido a la gestión de crisis de salud causada por el COVID-19, tuve que realizar el TFG en casa, convirtiendo el trabajo en una investigación bibliográfica.

Resumo

O obxectivo do meu TFG é a planificación do desenvolvemento e caracterización de novos materiais que consisten en polímeros con propiedades mecánicas, térmicas e de barreira melloradas, usando principalmente nanocelulosa como reforzo. Céntrase no estudo e a modificación química da superficie da nanocelulosa, para mellorar a compatibilidade cos polímeros. Á súa vez, estudaranse modificacións para os polímeros. O obxectivo é lograr materiais con características apropiadas, mellorando a relación entre a matriz e a fase dispersa. Cando esta compatibilidade se alcance para ambas partes, polímeros e nanocelulosa, crearanse os “composites”. Ademais, as porcentaxes de cada parte variarán para mellorar as propiedades do polímero. Os materiais finais terán aplicacións tales como o envasado de alimentos, tapadeiras, pezas de automóbiles, bolsas reutilizables, bandexas e contedores, xoguetes, artigos para o fogar e materiais de construción, entre outros.

Este TFG céntrase no estudo bibliográfico dos materiais, estratexias e técnicas a desenvolver. Cómpre mencionar que este TFG é o resultados da modificación da proposta inicial que incluía principalmente traballos experimentais na empresa CETIM. O desenvolvemento do proxecto foi interrompido pola situación excepcional da COVID-19. Despois da publicación do Real Decreto 463/2020, o 14 de marzo, que declarou o estado de alarma debido á xestión da crise de saúde causada pola COVID-19, tiveron que facer o TFG na casa, convertendo o traballo nunha investigación bibliográfica.

1. Introduction

1.1. Foreword^{1 2 3 4}

The most used polymer on Earth, cellulose in form of nanocellulose, is selected as the preferred natural reinforcer to develop composites. The main reason is its appealing properties: environmentally friendly, renewable and biodegradable. The motivation of this project emerges from the idea of the improvement of existent polymers with this natural compound in nanometric size: nanocellulose. It combines the inherent properties of cellulose with the ones regarding nanometric size: large surface area, firmness, high reactivity, hydrophilicity, chirality and lightness. It will give nanocellulose high added value, making it ideal raw material for a wide variety of industrial applications, specifically for the study of composites.

Besides nanocellulose, composites can also have microcellulose and their derivatives as a reinforcement. The polymeric matrix will vary from conventional thermoplastics like polypropylene (PP) and polyethylene (PE) to biopolymers, that is, polymers produced from natural resources or biosynthesized by living organisms, like polylactic acid (PLA). In addition, bio-based polymers will be studied as possible matrices for composites. However, cellulose and polymeric matrix have a lack of compatibility in their structures due to polarity differences. Because of their hydrophilic nature, is always a challenge to mix cellulose micro or nanofibres with hydrophobic polymers. The key point is to reduce the surface energy of nanocellulose to improve the dispersibility and compatibility with hydrophobic matrices. Fortunately, nanocellulose surface is very reactive because of its hydroxy groups and it can be modified on demand. Different functionalities can be added to nanocellulose mainly by covalent functionalization, involving reactive hydroxy groups from the surface. Hydrolysis, esterification and silylation are some of the modifications that can be done to nanocellulose. Also, polymer surface modification can be produced by grafting processes using different coupling agents.

These modifications will improve several characteristics of the composites, not only because nanometric size of nanocellulose produce unique properties, but also due to the combination of both phases. Regarding mechanical properties, the composites obtained will have higher stiffness and higher tensile modulus, that is, the stress they are able to handle will be higher regarding the polymer alone. In terms of thermal stability, it

¹ (H.P.S. Abdul Khalil, A.H. Bhat, A.F. Ireana Yusra) Green composites from sustainable cellulose nanofibrils; *Carbohydr. Polym.* **2012**, 87, p 963-979.

² (Mittal Vickas) Barrier properties of composite materials; **2009**; p.1-17

³ (Alain Dufresne) Cellulose nanomaterial reinforced polymer nanocomposites; *Curr. Opin. Colloid Interface Sci.*; **2017**; 27; P.1-8. DOI: <http://dx.doi.org/10.1016/j.cocis.2017.01.004>

⁴ Information from: Plasticseurope.org; https://www.plasticseurope.org/download_file/force/3570/632

will be increased when combining both phases. Last but not least, barrier properties will be modified. They are related with the distinction in microstructure of the polymer material. Normally, materials are designed to improve mechanical and thermal properties, thus neglecting barrier ones. It is assumed that enhancing mechanical properties, barrier properties will be consequently improved, but it is not always the case. The control on barrier properties will let us to control some functions of the composites that could be interesting in some fields.

For you to know the impact of this research, *Figure 1⁴* shows the annual global production of polymers:

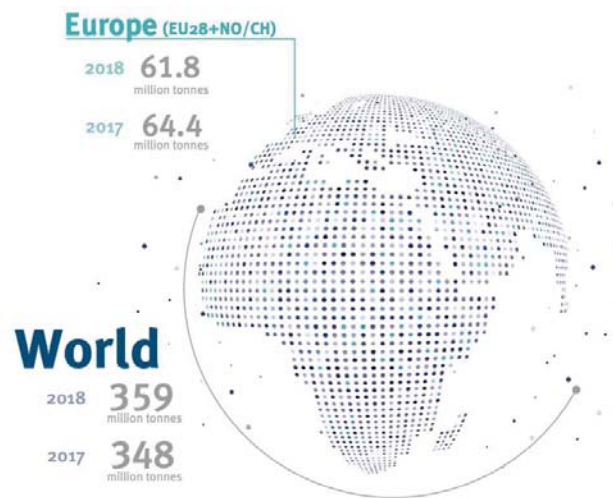


Figure 1: Global and European production of polymers in 2018. Includes Thermoplastics, Polyurethanes, Thermosets, Elastomers, Adhesives, Coatings and Sealants and PP-fibers.

This fact leads us to think of the importance of thermoplastics and other polymers in our daily lives. Thermoplastics demand in 2018 in Europe was mainly represented by packaging and building and construction markets, with the 39,9% and 19,8% respectively (*Figure 2⁴*).



Figure 2: Thermoplastics demand by segment on 2018.

Regarding the resin types of polymeric polyolefins (thermoplastics), PP and PE represent the 49% of the total demand (Figure 3⁴).

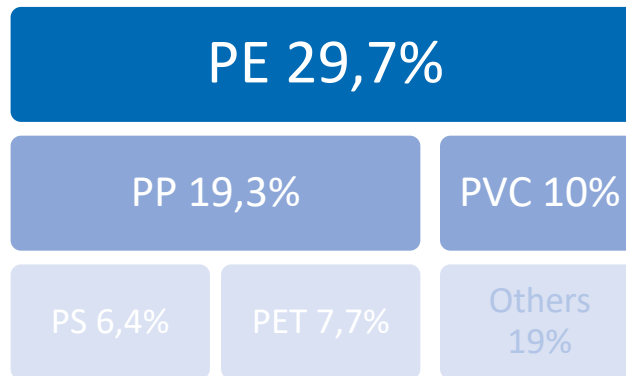


Figure 3: Plastic demand distribution by resin types in 2018.

Another important reason for the development of this project is the longevity of polymers. Regarding thermoplastics materials their life cycle (Figure 4⁴) depends on the thermoplastic itself. Some of them have a lifespan of less than one year, but other can last 50 years or more.

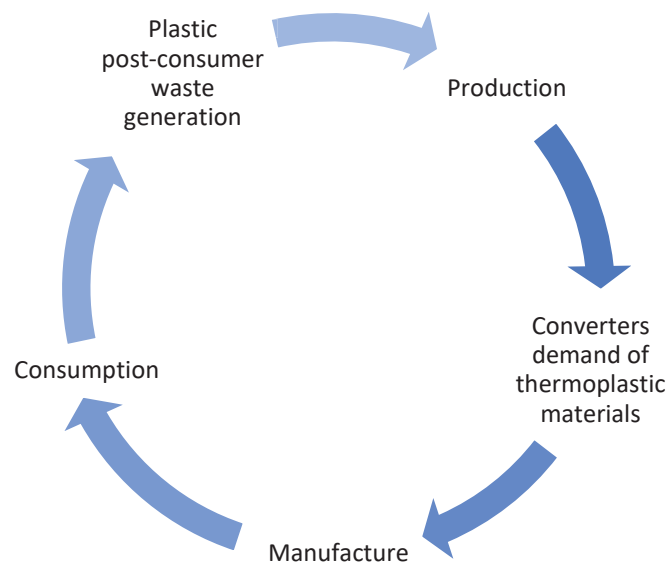


Figure 4: Life cycle of thermoplastics products.

From the production of thermoplastics to their waste they show different uses and value options. Waste generated can be collected and be recycled, be used for energy recovery or be disposed at the landfill. The percentages are 32,5%, 42,6% and 24,9% respectively. In relation with this project, if the percentage of polymers could be reduced by addition of natural compounds such as nanocellulose, the overall waste created by thermoplastics will decrease and some other uses could be evaluated for these new materials.

1.2. Company information⁵

I was working on my final project with CETIM company. It is a technological centre of research, located in Alvedros industrial park (A Coruña). It has 6 different laboratories where all the projects take place: chemistry, microbiology, auxiliary, climatic chamber, industrial and construction.

The centre possesses four fields of knowledge:



Advanced materials are traditional materials whose properties have been enhanced. In this field valorisation, extraction and physic-chemical modifications of wood derivatives are studied, mainly centred in cellulose and lignin. High added value and eco-friendly materials from lignocellulosic derivatives are developed: polymers, ligands, coatings, additives, paper...

I did a project related to 'Advanced materials'. The materials studied are utilized in high-technology applications, that is, devices or products that operate using relatively intricate and sophisticated principles.

Broadly speaking, in my TFG I have studied new generations of micro and nanocellulose development and its chemical modifications, and also new thermoplastics and their modifications.

Before Covid-19 lockdown, I was working in the project at the CETIM installations. In fact, I was there one week, and I prepared nanocellulose from cellulose pulp. Also, I carried several reactions such as silylation of nanocellulose so as increase its hydrophobic character to be compatible with polymeric matrices. However, these tasks were interrupted in March 14th and I continued my work as a bibliographic research at home, while the project was being developed by the CETIM. So, this information could be useful in the future development of CETIM projects.

⁵ General information of CETIM from: <http://cetim.es>. Visit data: 13/04/20.

2. Composites⁶

A composite is whatever multiphase material artificially made, which exhibits a significant proportion of the properties of the different constituent phases. According to the ‘principle of combined action’, better properties are shown by combination of two or more different materials. Many modern applications require materials with certain properties that are not present in the conventional metal alloys, ceramics or polymers. This is the reason why composites are formed, to create extraordinary materials.

Composites are mainly composed of two phases, one is called the **matrix**, which is continuous and surrounds the other phase called **dispersed phase**.

The properties of the composites will depend on the properties of the matrix and dispersed phase: the relative amounts of both phases, the geometry of dispersed phase, that is, particle size, distribution and orientation along the matrix and the degree of cohesion between the phases.

Composites can be classified in three main groups regarding **dispersed phase** types: particle-reinforced, fibre-reinforced and structural composites.

Figure 5⁷ shows at least two subdivisions for each group.

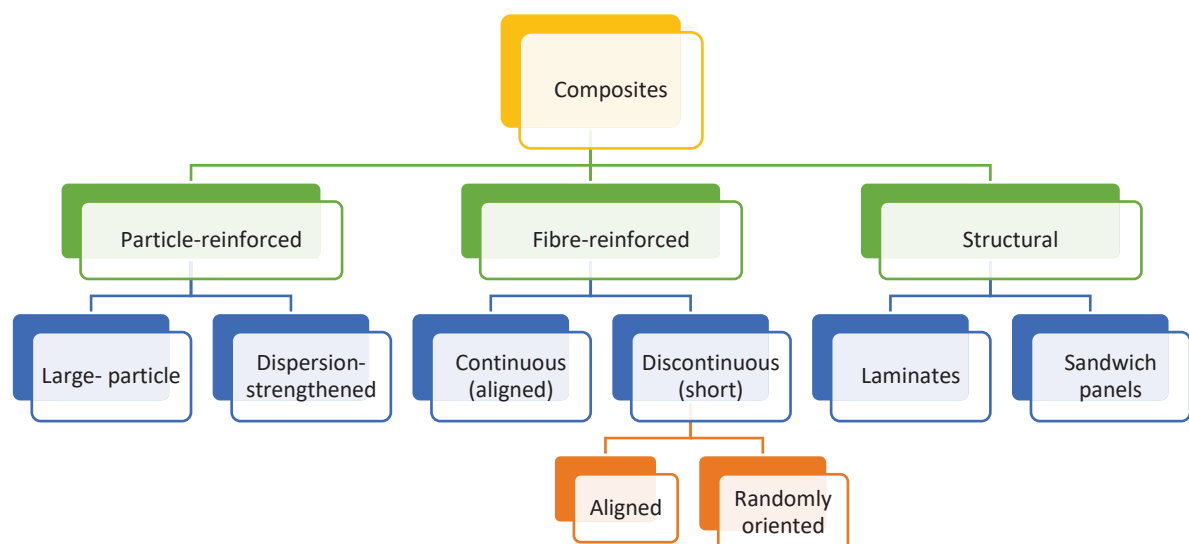


Figure 5: Classification of composites types regarding dispersed phase.

⁶ (William D. Callister, Jr) *Materials Science and Engineering*; Seventh edition; Joseph Hayton; University of Utah; EE. UU; 2007; p 577-600.

⁷ Own elaboration adapted from: (William D. Callister, Jr) *Materials Science and Engineering*; Seventh edition; Joseph Hayton; University of Utah; EE. UU; 2007; p 579.

To begin with **particle-reinforced composites**, they are classified in large particle and dispersion strengthened composites. The main difference lies in the reinforcement or strengthening mechanism. In large particle composites the particle phase is harder and stiffer than the matrix, and they block matrix movement. Summarising, the particles bear a fraction of the load, from the stress applied from the matrix. An example of large-particle composite is concrete, where the matrix and the dispersed phase are both ceramic materials. For dispersion-strengthened composites, particles are smaller with diameters between 0,01 and 0,1 μm . The matrix stands the major portion of the applied load and the particles hinder the dislocations in the composites.

Secondly, **fibre-reinforced composites** are the most important, technologically speaking. The dispersed phase is in form of a fibre. The differences between the classification lie in the specific strength and mechanical parameters of final composites. They are classified according to fibre length (*Figure 5*) in continuous and discontinuous fibres reinforced composites. In addition, *Figure 6*⁶ present various geometrical and spatial characteristics of fibres that may influence the composite properties.

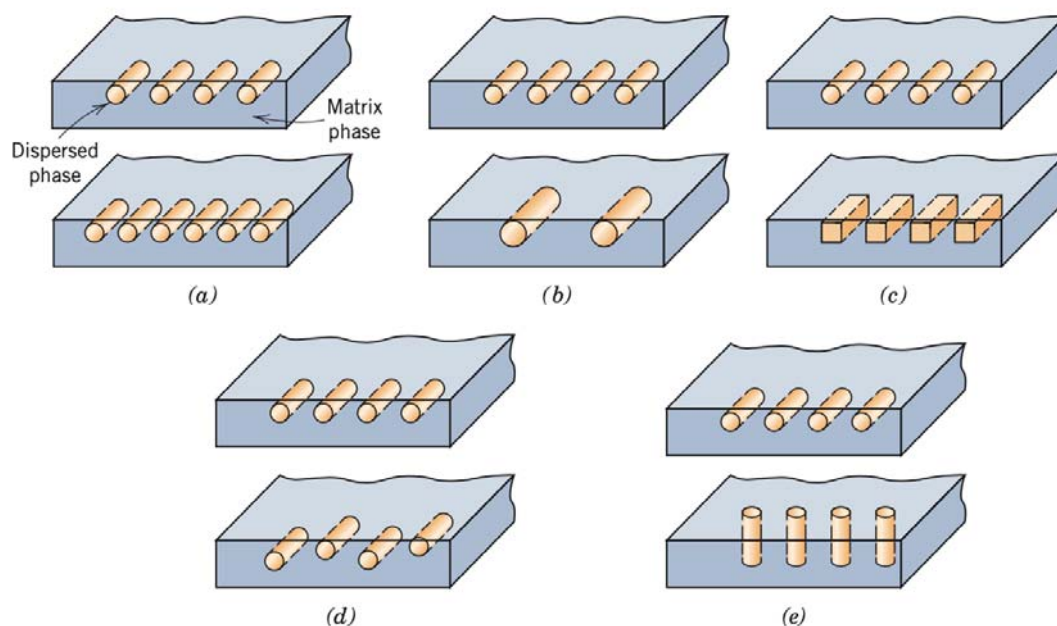


Figure 6: Schematic representations of various geometrical and spatial characteristics of particles of the dispersed phase that may influence the properties of composites.

(a) concentration, (b) size, (c) shape, (d) distribution, and (e) orientation.

The fibres can be divided in whiskers, fibres and wires regarding their size:

- Whiskers are very thin crystals with large length-to-diameter ratios. They present a high degree of crystallinity and high strength.
- Fibres are polycrystalline or amorphous and have small diameters. They are normally present in polymer or ceramic composites.
- Wires have relatively large diameters, and they are extensively introduced in metallic composites and alloys such as molybdenum, tungsten and steel.

Finally, **structural composites** are formed of both homogeneous and composite materials. Their properties depend on the constituent materials and the geometric arrangement. Laminar and sandwich panels are two most common structural composites (*Figure 5*). Laminar composites are composed of two-dimensional sheets or panels. They have a preferred high-strength direction, and the layers are stacked and cemented together. Sandwich panels consist of two outer sheets bonded to a core. The outer sheet is formed of relatively stiff and strong materials while the core is lightweight and present low resistance to deformation.

In general, composite **matrix phase** can be metallic, polymeric or ceramic. This project research is focused on the reinforcement of polymers, specifically on thermoplastic polymers, not only conventional ones, but also bio-based. The dispersed phase in the composites that will be developed in this project is mainly nanocellulose. This compound will be in form of fibres and particles, so we will talk about particles and fibres reinforced composites for the next aspects.

The polymers improved properties, due to the formation of composites, will be discussed in more detail later in *section: 3.7*, but we look mainly for the improvement of their behaviour through stress, temperature and barrier properties.

2.1. Processed techniques of composites⁸

Polymeric-matrix composites with dispersed nanocellulose can be prepared and processed by different methods. The functionalization of both components is very important and will be addressed later in *sections: 3.6 and 4.1*. The processing techniques will also have a great influence on the final material properties.

The main problem to face at the processing is the particle dispersion in the matrix, because of the natural tendency of dispersed phase to agglomerate. To avoid it, solvent processes can be used, maintaining particles suspension in a solvent. This process will improve matrix-filler compatibility. Alternatively, it is possible to create steric barriers among particles and increase interparticle distances with melting processes.

I will start describing the most important techniques found in the bibliography about processing nanocellulose particles-reinforced polymeric composites (*Figure 7*⁹). Although particles and fibres are different dispersed phases, almost all of these techniques can be used for both types. Later in *sections: 4.2 and 4.3* different polymeric composites are studied taking into account these techniques.

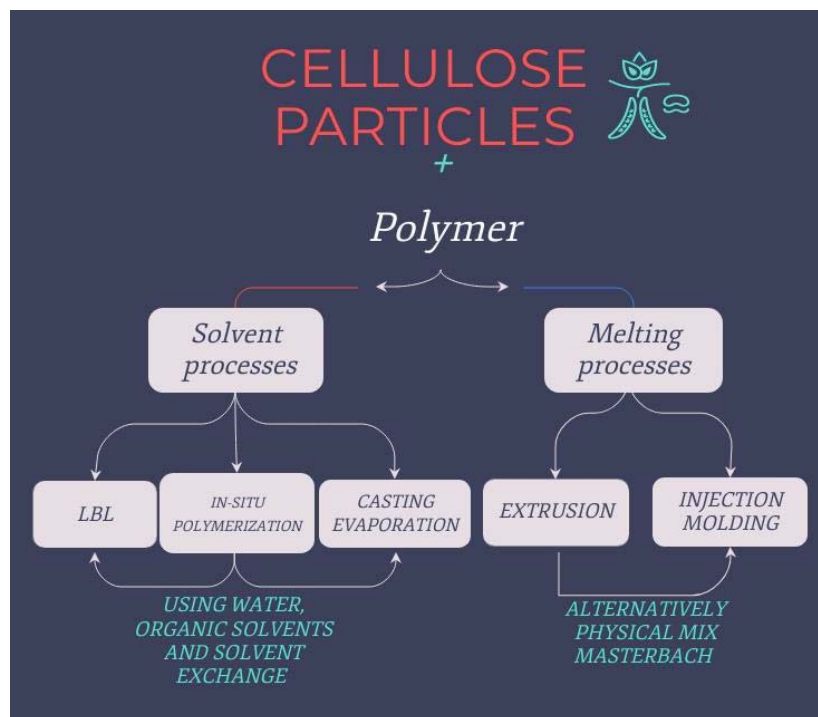


Figure 7: Methods of inclusion of cellulose dispersed particles in a polymer matrix phase.

⁸(Hanieh Kargarzadeh Mariano M, Jin Huang, Ning Lin, Ishak Ahmad, Alain Dufresne, Sabu Thomas) Recent developments on nanocellulose reinforced polymer nanocomposites; *Polymer*; 2017, 132, p 368-393. DOI: <https://doi.org/10.1016/j.polymer.2017.09.043>

⁹ Own elaboration adapted from: Recent developments on nanocellulose reinforced polymer nanocomposites; *Polymer*; 2017, 132, p 371. DOI: <https://doi.org/10.1016/j.polymer.2017.09.043>

In melting processes, no solvents are involved and time consumed is relatively small. However, sometimes this method cannot be used because the phases present incompatibilities. There are two modalities of melting processes, injection molding and extrusion.

Extrusion is performed in an extruder (*Image 1¹⁰*) by mixing two solid components (polymer and nanocellulose in this project). Both are mixed under shear, combining screws and temperature. Extrusion enhance the dispersion by mechanical stress applied though the screw. The lower the shear melt-mixing the less damage is done to the particle structure. Extrusion parameters are crucial. The main function of the screw is to transfer the polymer from the feed hopper to the material mixing area.

Some problems such as the reduction of the size of the nanoparticles by breaking them due to shear action, can be caused by extrusion. Extrusion screws are normally tight. Consequently, the pressure and temperature on the polymer increase as the result of the friction. It is important to determine screws speed and temperature to avoid overheating and overshearing.

It is proved that in a system where particle-particle interactions are stronger than particle-polymer interactions, some particles can degrade the mechanical properties of the composite. To avoid that, different chemical modifications of both phases should be performed in order to increase polymer-particle compatibility that will be discussed later in *sections: 3.6.3 and 4.1*.



Image 1: Mini extrusion machine from CETIM.

¹⁰ Own elaboration from my stay in CETIM.

Injection molding is a solid-state process suitable for polymers that present granule and fibre geometry that can be mixed and heated.

Before injection molding, extrusion or masterbatch of both phases is carried, to ensure the dispersion of nanocellulose among the polymer. An injection pump (*Image 2*¹⁰) is coupled to the outlet nozzle of extrusion machine (*Image 1*), letting the melting material go inside it. From the pump, the materials are transported into the mold cavity using air pressure.

The conditions of pressure and temperature of the injection pump are controlled to provide good composites. Injection temperature is an essential parameter because it may affect the viscosity of the melted polymer and the nanoparticles order can be altered modifying the final properties.

The reproducibility of injection molding is optima. Unfortunately, some thermoplastic materials need higher temperatures to be melt and injected and high temperatures may damage cellulose nanoparticles.

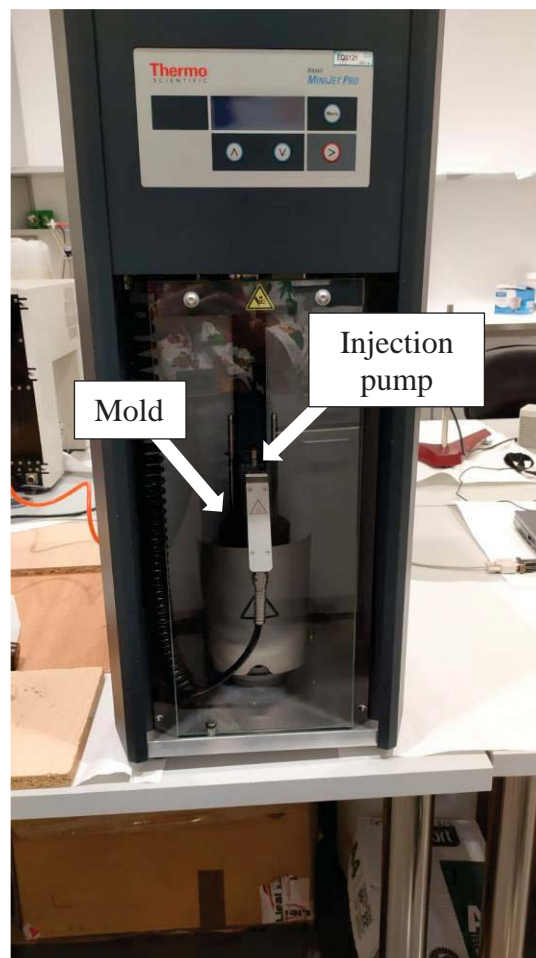


Image 2: Mini injection molding machine from CETIM.

In solvent processes (*Figure 7*), **casting and evaporation** are used to obtain films (type of composite, regarding geometry) after solvent removal by evaporation. This method is limited to laboratory scale. The first step is the suspension of the matrix polymers and nanoparticles in appropriate solvents. The properties of the suspensions can be controlled by their charge. Solvent evaporation occurs in a long time period.

Matrices that are used with this technique do not need to be hydro soluble (water dispersible). The use of high-speed stirring during polymer dissolution may cause chain scission.

Even with limitations, interesting materials can be formed. Young modulus, that is, a parameter that measure the stiffness of the material and roughness of the film, increase. Hydrophobic polymeric matrices require more tedious procedure, such as solvent exchange from water to acetone and sequentially to a suitable organic solvent. The use of DMF (Dimethylformaldehyde), pyridine, toluene and chloroform increase the number of polymers suitable for this method.

In-situ polymerization is normally used in adequate solvents where monomers that form the polymer are soluble and particles can be dispersed. The requirements for the solvent limit the use of this technique in the industry. Some restrictions derivate from the amount of nanoparticles that can be efficiently dispersed. The presence of nanoparticles modifies the viscosity of the system, increasing reaction time of polymerization process.

Hand laminating, or **layer by layer (LBL) laminating**, is a method where intercalated layers of different compounds are produced by hand or using spray. The combination of the layer properties can provide superior surface and mechanical properties. The desired characteristics depend on the number of layers, pH, ionic strength and polymerization degree. Generally, aqueous media is used to disperse layers of opposite charge alternatively.

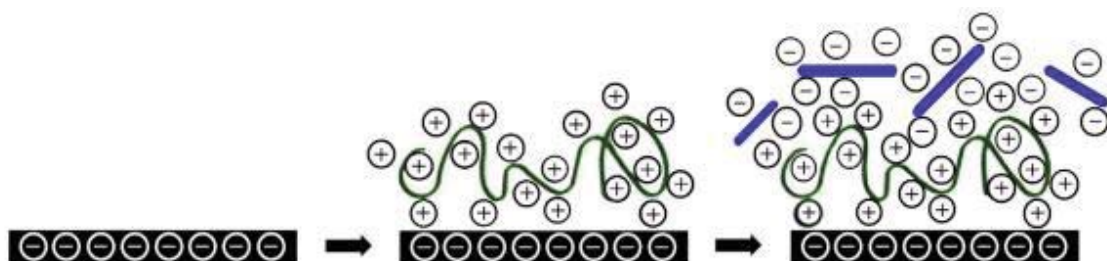


Figure 8: LBL explanation with charged polymer and cellulose nanoparticles.

Figure 8⁸ shows interactions of nanoparticles with charged polymers during a LBL deposition. Humidity is crucial to the properties of the composites formed, in this case films. The presence of water can modify the interlayer interactions, causing the decrease in the Young modulus.

3. Micro/nanocellulose: Dispersed phase¹¹

As it has been explained, the dispersed phase in the project is cellulose, mainly as **micro** and **nanocellulose**. Undoubtedly, cellulose plays an important role in structural part of plants. It uses as reinforcement in composites are an extension of its role in nature. Before presenting types and modifications, let's describe cellulose.

3.1. Structure of cellulose^{12 13}

Cellulose is a linear, stereoregular, semi crystalline polysaccharide composed of D-glucopyranosic units bonded by chemical β -1,4-glycosidic links, as it can be seen in *Figure 9*¹⁴. The glucopyranosic units have a "chair" conformation. Each glucopyranosic unit of cellulose contains three hydroxyl functional groups: a primary group and two secondary group and they both increase hydrophilicity and sorption of the compound.

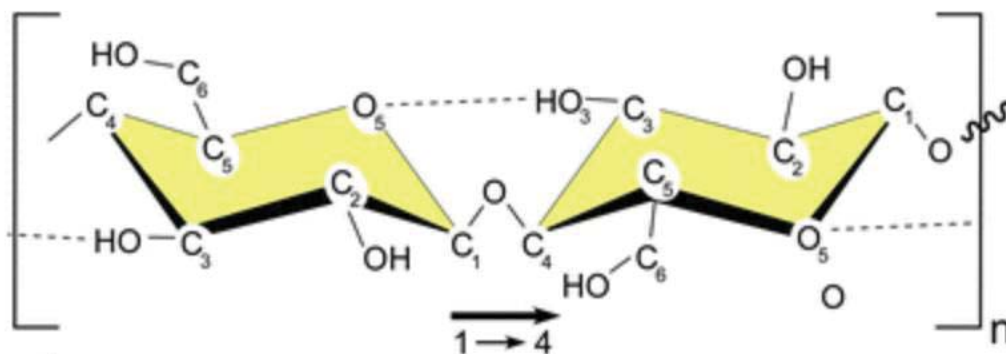


Figure 9: Cellulose structure

The β (1 \rightarrow 4) linkage allows favourable intramolecular hydrogen bonds interactions O₃H...O₅, as it can be seen in *Figure 9*, resulting in a pseudo helical conformation of cellulose chains. They present different torsion angles and the changes in these parameters cause different intra and intermolecular hydrogen bonds between neighbouring chains, becoming viable to different conformations.

¹¹(loelovich M) Cellulose: nanostructured natural polymer; 2014, Israel; p 1-5

<https://www.researchgate.net/publication/260965048>

¹² (Hebert L.R); PI 0906117-7 A2, date of patent: 16/07/2013

¹³ (Koon-Yang L; Yvonne A; Lars A.B; Oksman K; Bismarck A) On the use of nanocellulose as reinforcement in polymer matrix composites; *Compos. Sci. Technol.* **2014**, 105, p 15-27.

DOI: <https://doi.org/10.1016/j.compscitech.2014.08.032>

¹⁴ (Robert J. Moon, Ashlie Martini, John Nairn, John Simonsen, Jeff Youngblood) Cellulose nanomaterials review: structure, properties and nanocomposites; *Chem. Soc. Rev.* **2011**, issue 7., DOI: <https://doi.org/10.1039/C0CS00108B>

3.2. Cellulose crystallinity¹⁴

Cellulose has several polymorphs (I, II, III, IV). Cellulose I is crystalline and is produced by primitive organisms, such as algae or bacteria. It is usually known as 'natural' cellulose. Cellulose II is the most stable cellulose structure and has an important technical relevance. Cellulose III can be formed from cellulose I and II by ammonia treatments and if cellulose III is treated with heat, cellulose IV is obtained.

Focusing on cellulose I, it has two polymorphs that can be seen in *Figure 10*¹⁵.

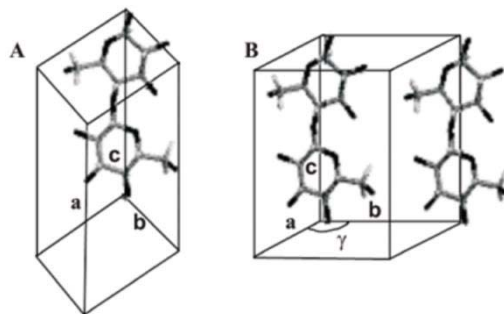


Figure 10: Schematic representation of packing in unit cell of cellulose I. (A) Triclinic unit cell: I_{α} (B) Monoclinic unit cell: I_{β} . Monoclinic angle is obtuse.

I_{α} has a triclinic structure and I_{β} monoclinic one. They can coexist together in various proportion depending on the cellulose origin. Mainly I_{α} phase is found in cellulose produced by primitive organisms, and I_{β} is produced by plants and marine animals.

3.3. Sources of cellulose¹

The main sources of cellulose are plants. Herbaceous plants contain 30-40% of cellulose, in woods there are 45-50%, in bast plants (flax, ramie etc.) 60-70%, and in cotton fibres 90%. It is also found in marine animals, algae, fungi, bacteria invertebrates and amoeba. In most organisms, cellulose is present as a component of cell walls. Nevertheless, the main commercial source of cellulose is wood.

*Figure 11*¹ shows the natural origin of cellulose from wood sources.

¹⁵ (Reginaldo A. Festucci-Buselli I; Wagner C. Otoni I; Chandrashekar P. Joshi II) Structure, organization, and functions of cellulose synthase complexes in plants. *Brazilian Journ. Of Plants Physiology*; **2007**, (19) DOI: <https://doi.org/10.1590/S1677-04202007000100001>

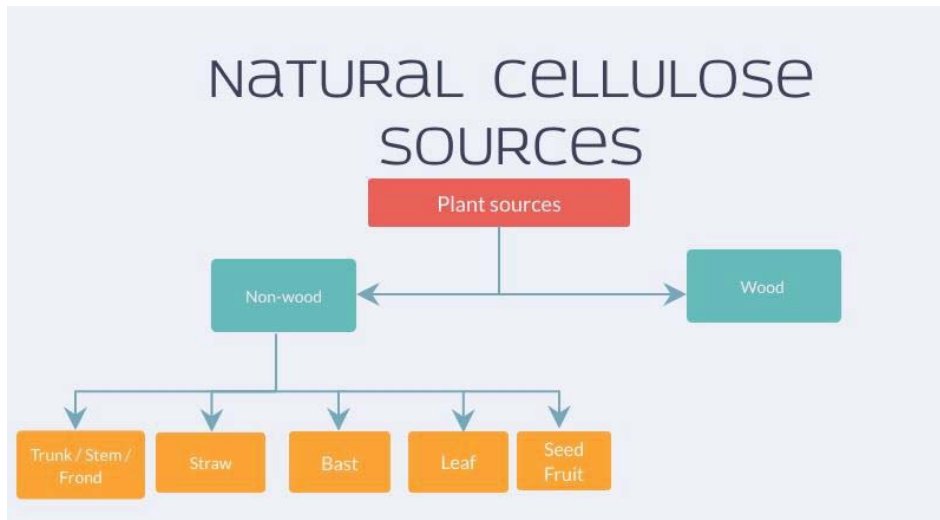


Figure 11: Natural sources of cellulose.

3.4. Nanocellulose¹⁶

As I commented before, cellulose will be used mainly as **nanocellulose**, in form of nanofibrils (CNF) and nanocrystals (CNC) in the composites. These nanoparticles contain amorphous and crystalline regions that can be isolated from the cellulose source by mechanical, chemical or enzymatical processes, which will be treated in *section*: 3.6.2.

CNF are fibrils with lengths and widths in micrometre and nanometre scales. CNC has smaller aspect ratio and they are prepared by acid hydrolysis degrading amorphous regions and yielding the crystalline cellulose nanoparticles. The differences between CNC and CNF are illustrated in *Figure 12*¹⁶.

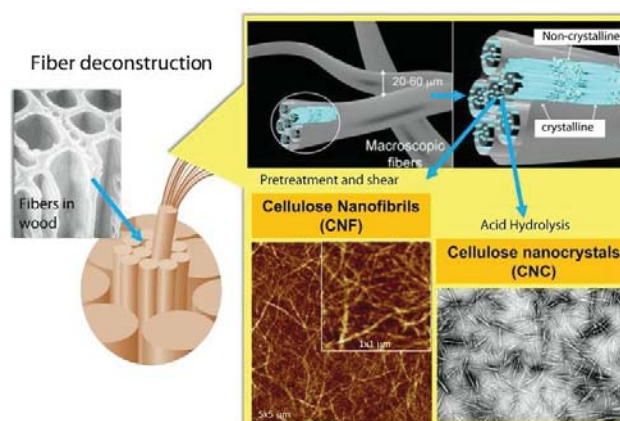


Figure 12: Schematic illustration of CNF and CNC production from fibre cell walls by mechanical and chemical treatments.

¹⁶ (Carlos Salas, Tiina Nypelo, Carlos Rodriguez-Abreu, Carlos Carrillo, Orlando J Rojas) Nanocellulose properties and applications in colloids and interfaces; *Curr. Opin. Colloid Interface Sci*; **2014**; 19, p.383-396. DOI: <https://doi.org/10.1016/j.cocis.2014.10.003>

The majority of the properties of cellulose such as: specific weight, melting point, parameters of crystalline unit cell and others, can be considered as constant of a given sample. Nevertheless, when decreasing the size to the nanoscale, the specific surface increases, thus reactivity. In addition, nanocellulose shows exclusive properties like biodegradability, high aspect ratio, low density, high strength and stiffness.

Cellulose was firstly discovered after isolating it from plants. During delignification of cellulose (removal of lignin from woody tissue) at high temperatures, nanofibrils are released from the ligno-carbohydrate cellulose matrix, present in the cellular wall of plants¹⁷. Delignification is explained in *section: 3.6.1.1*, when pre-treatment of native cellulose is developed.

Overall, the linear cellulose macromolecules are formed of fibres with crystalline and non-crystalline domains and elementary nanofibrils, joined each other by hydrogen bonds, which are aggregated into bundles called microfibrils. This is clearly seen in *Figure 13*¹⁸.

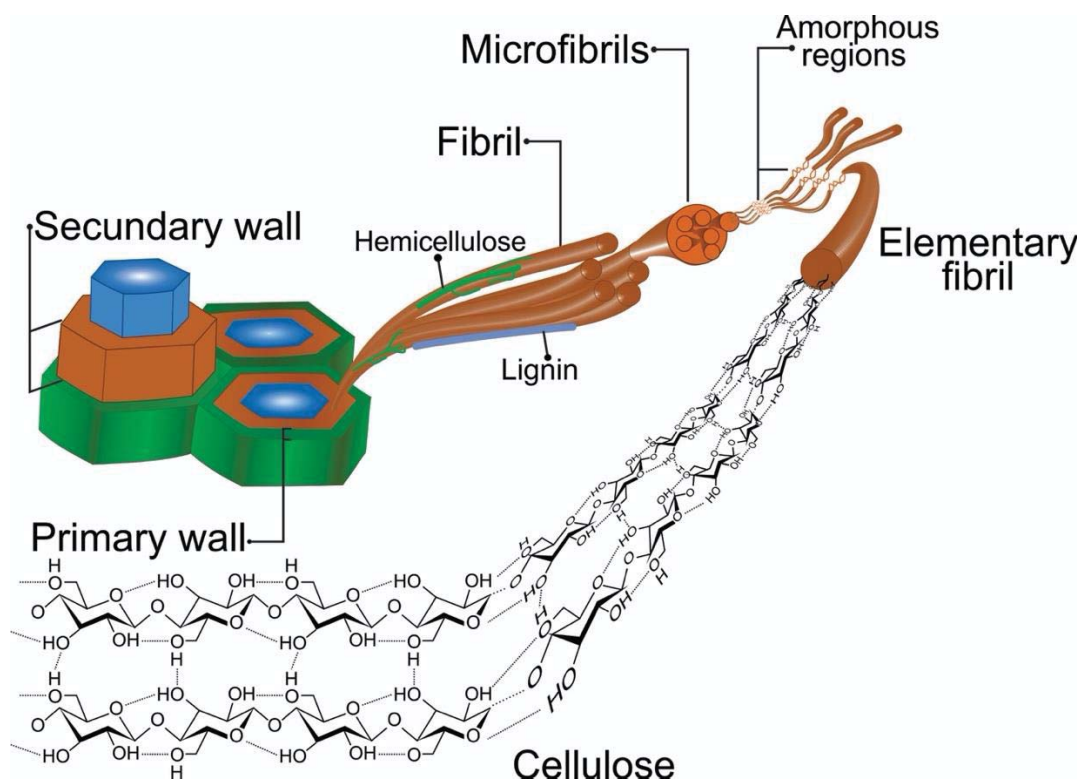


Figure 13: Cellulose organization in plants cell walls

¹⁷ (Bo Jiang, Chaoji Chen, Zhiqiang Liang, Shuaiming He, Yudi Kuang, Jianwei Song, Ruiyu Mi, Gegu Chen, Miaolun Jiao, Liangbing Hu) Lignin as a Wood-Inspired Binder for Plastic Replacement; *Adv. Funct. Mater.* **2019**; (30) 4. DOI: <https://doi.org/10.1002/adfm.201906307>

¹⁸ (John Rojas, Mauricio Bedoya and Yhors Ciro) Current Trends in the Production of Cellulose Nanoparticles and Nanocomposites for Biomedical Applications; **2015** DOI: 10.5772/61334

3.5. Nanocellulose types¹¹

Since cellulose has a nanostructured organization, the isolation of free constituents such as nano and microfibrils, nano and micro crystals and nano and micro filaments is promoted. This section develops types of nanocelluloses that can be obtained from natural cellulose.

3.5.1. Bacterial nanocellulose¹¹

Bacterial nanocellulose (BNC) has unique properties produced by several species of fermentation bacteria, such as *Gluconacetobacter xylinus*. The forming long and thin nanofibrils are aggregated to flat microfibrils. The neighbouring microfibrils interlace forming bands and their structure are filled with water. This nanocellulose contains about 80% of I_α crystalline allomorph and its crystallites large size is 7-10 nm.

- The main application is in cosmetic field as a moistening mask and as an ingredient of moistening cream due to its high-water content. However, it can also be used in veterinary and biomedicine implants.

3.5.2. Nano fibrillated cellulose¹¹

Nano fibrillated cellulose (NFC) results from grinding diluted cellulose pulp suspension in a high-pressure mill, that is a mechanical treatment that will be explained in *section: 3.6.2.1*. The NFC typically consists of disintegrated microfibrillar bundles with diameters of 10-30 nm. There is a major drawback in the commercialization of NFC: the high energy consumption linked to mechanical disintegration of the fibres to nanofibres. In order to decrease the energy consumption during the mechanical process, it is preliminary modified by chemical hydrolysis with acids or enzymes.

- Main application areas of NFC are reinforcing additives to paper, polymers and other composite materials.

3.5.3. Cellulose nanocrystals¹¹

Cellulose nanocrystals (CNC) can be made by hydrolysis of cellulose samples with concentrated solutions of sulfuric or hydrochloric acids at moderate temperatures and following the mechanical or ultrasound disintegrations of the acid-treated cellulose in water. To isolate CNC with increased yield (67-70 %), hydrolysis with 57-60% wt sulfuric acid is done at 45°C for 1 hour. The width of CNC is 10-20 nm. Due to its highly crystalline structure, CNC has an increased specific gravity, low hydrophilicity and accessibility.

These particles exhibit unique properties such as high-magnetic response, high strength and large surface area. However, the aspect ratio of the particles is lower regarding nano fibrillated cellulose.

- The applications are the filling of glues, coatings composition and paints.

3.5.4. Amorphous nanoparticles¹¹

To isolate the amorphous nanoparticles (ANP) with the optimal yield (65-67%), it is proposed to treat the cellulose with cold 65-66% wt sulfuric acid in combination with disintegration. Generation mechanism of amorphous nanoparticles consists in depolymerization, sulfonation and dissolving cellulose in concentrated sulfuric acid, then the amorphous flocs are regenerated and grinded in water medium. The average diameter of the spherical ANP is 100nm. It is characterized by high degree of amorphous and a great number of sulfonic groups. Due to amorphous structure the ANP acquire such specific features like increased content of functional groups, high accessibility, enhanced sorption ability and hydrophilicity, high viscosity and thickening ability.

- When increasing acidic functional groups content in ANP, some therapeutically active substances became immobilized, and this is the reason why its main application is immobilization of biological active substances and drugs. It is also used as filler and thickener of cosmetic and medicine remedies, pastes, creams, sprays, etc.

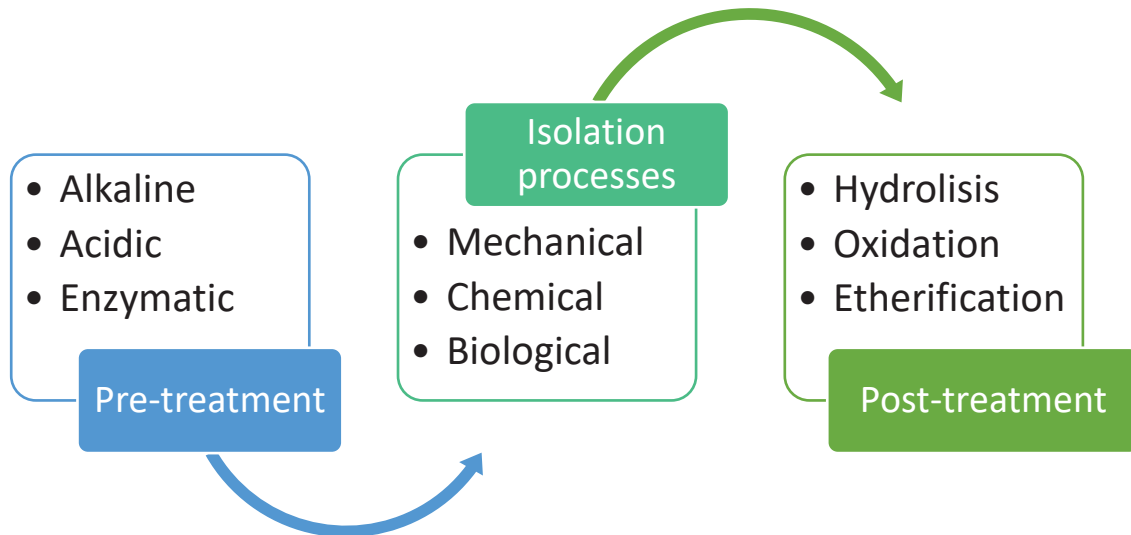
In *Table 1*, the information above is collected. The choose of nanocellulose type in the composites, will depend on the application and purpose of the new material.

Table 1: Review over types of cellulose and their characteristics.

Type	Produced by...	Diameter (nm)	Common Applications
BNC	Fermentation bacteria	7-10	Cosmetics
NFC	Grinding pulp suspension in pressure mill	10-30	Additives Composites
CNC	Acid hydrolysis of native cellulose	10-20	Glues Paints Coatings
ANP	Depolymerization and acid treatment of pulp	100	Biological interest Medicine

3.6. Nanocellulose treatments: From Nature to the lab¹⁹

Before creating composites, cellulose become a large ride, passing through different treatments. They are necessary to obtain nanocellulose ready for inclusion in polymeric matrices. The steps that cellulose biomass has to follow are:



3.6.1. Pre-treatments^{20 21}

Cellulose is manufactured from different sources of raw materials. As I commented before in *section: 3.3*, the most important is wood, mainly from forest. In addition, cellulose is also present in agriculture residues, water plants, grasses and other plants substances.

In wood, cellulose is present in plants secondary wall. Cellulose from agricultural origin is located in the primary wall, thus is easier to obtain. It is graphically represented in *Figure 13*. Regardless of the source, raw cellulosic materials need to be treated to obtain nanocellulose. Firstly, I will comment the pre-treatments found in the bibliography, from which we obtain cellulose pulp.

3.6.1.1. Alkaline pre-treatment process

The alkaline process (pulping and bleaching), also called delignification, consist of degradation of lignin using a NaOH solution and after water. The aim of this step is the

¹⁹ (Nathalie Lvoine, Isabelle Desloges, Aline Defresne, Julien Bras) Microfibrillated cellulose-Its barrier properties and applications in cellulosic materials; *Carbohydr. Polym.*; **2012**; 90; p.735-764. DOI: <https://doi.org/10.1016/j.carbpol.2012.05.026>

²⁰ Bio-based Polymers and Composites; (Editors: Muhammed Laming Sanyang, Mohammed Jawaid) Switzerland; **2019**; p.71-73. DOI: <https://doi.org/10.1007/978-3-030-05825-8>

²¹ (Patchiya Phanthong, Prasert Reubroycharoen, Xiaogang Hao, Guangwen Xu, Abuliti Abudula, Guoqing Guan) Nanocellulose: Extraction and application. *Carbon Resources Conversion*; **2018**; 1 p.32-43 DOI: <https://doi.org/10.1016/j.crcn.2018.05.004>

degradation of the bonds between lignin and carboxylates that creates the wood biomass. This reaction is represented in *Figure 14*¹⁷.

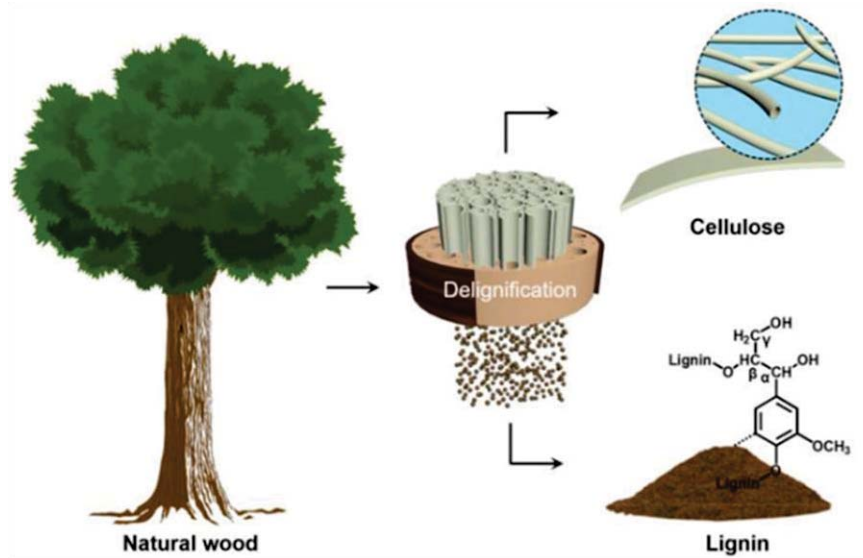


Figure 14: Cellulose and lignin from wood sources.

3.6.1.2. Bleaching pre-treatment

Alkaline process doesn't produce the total degradation of the linkages. Bleaching process remedy this matter. It consists of eliminating the rest of lignin and impurities from the cellulose pulp. The process can be done with hydrogen peroxides or chlorines.

There are other pre-treatments like acid or enzymatic ones. Basically, acid pre-treatment is used to enhance crystallinity of cellulose pulp and enzymatic one to modify lignin without disturbing cellulose for some interesting applications.

For this project, CETIM receive cellulose pulp already treated by an alkali or bleaching pre-treatment. Secondly in this section, I will comment the main processes to obtain cellulose particles from pre-treated cellulose found in the bibliography.

3.6.2. Isolation processes²¹

Cellulose pulp presents a macro structure, from where its derivatives can be isolated. The following methods in *Figure 15*²² are used to achieve the preferred morphology and structure of nanocellulose.

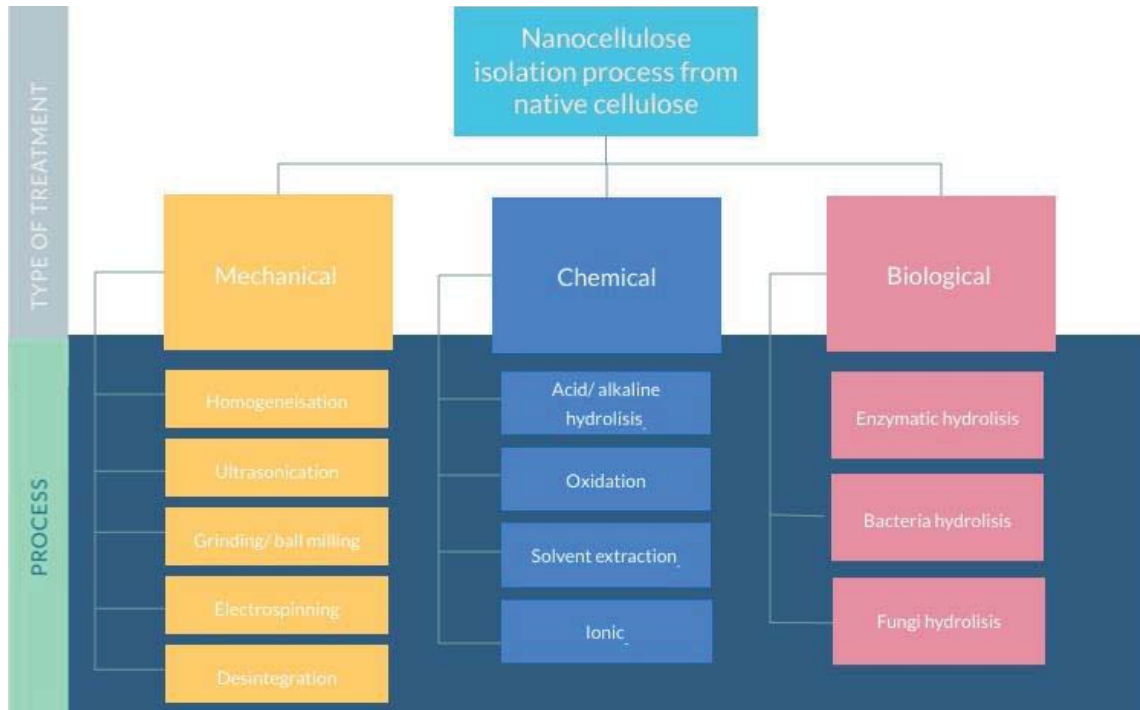


Figure 15: Main pre-treatments of cellulose to obtain nanocellulose..

They can be used separately or in sequence, combining on demand. Depending on the treatment used, nanocellulose can be obtained in its different typologies (*section: 3.5*).

3.6.2.1. Mechanical treatments

Mechanical treatments are carried out by applying high shear force to break cellulose fibres in nano fibrillated cellulose. Mainly, mechanical approaches include homogenization, ultrasonication and ball milling among others.

- In high pressure homogenization, cellulose is passed into a vessel with high velocity and pressure. Cleavage of cellulose is produced due to the impact and shear. Microfibrils are converted in nanofibrils with a diameter of 10-20 nm. During this process, inter and intramolecular hydrogen bonds are broken so the crystallinity of nanocellulose decreases. An example of one homogenizer that is used in CETIM is showed in *Image 3*¹⁰.

²² Own elaboration adapted from: (A.Tshikovhi, Shivani B. Mishra, Ajay K. Mishra) Nanocellulose-based composites for the removal of contaminants from wastewater; *Int. J. Biol. Macromol*; **2020**,152, p 618. DOI: <https://doi.org/10.1016/j.ijbiomac.2020.02.221>



Image 3: Homogenizer parts.

- Ultrasonication defibrates cellulose with hydrodynamic forces of ultrasound. The mechanical oscillations produced, creates gas bubbles, which are expanded and imploded.
- Ball milling can defibrillate cellulose fibres. Centrifugal forces from a rotating jar, produce shear forces among balls and the jar surface. As a consequence, fibrils are cracked, and their diameter is decreased.

3.6.2.2. Chemical treatments

Chemical treatments involve acids, bases and oxidants as chemical reagents. The main treatment is acid hydrolysis:

- Acid hydrolysis disperse nanocellulose as a stable colloid system. The combination of ordered and disordered regions in nanocellulose chains, facilitates the hydrolysis of the disordered ones with acids such as sulfuric acid. The most important factors in this process are reaction time, temperature and acid concentration. The main drawback is the use of acids, which leads to a washing step with cold water followed by centrifugation until neutral pH is reached. From acid hydrolysis CNC are obtained.

3.6.2.3. Biological treatments

Enzymatic hydrolysis is a method included in biological treatments. Enzymes are used to modify cellulose fibres. After enzymatic hydrolysis, a mechanical treatment is needed to obtain micro/nanocellulose. The treatment is performed in mild conditions. Nevertheless, long times are consumed. To reduce time, it is normally incorporated to other methods. Nanocellulose obtained has high crystallinity and thermal stability.

3.6.3. Post-treatment: nanocellulose modifications^{23 3}

Although nanocellulose present better properties in comparison with macro cellulose, there are disadvantages to face. To cite some of them: high moisture adsorption, poor wettability, incompatibility with most polymeric matrices and limitations in processing temperatures. These drawbacks encourage bibliographic research to focus on modifications of nanocellulose or polymer matrices to enhance their compatibility⁸. In addition, some reactions are carried out to reach desire properties by adding extra functionalities to cellulose particles. Mainly, this project is focused in increasing hydrophobic character of nanocellulose.

The main reactions, found in the bibliography, carried out on nanocellulose are:

- Hydrolysis
- Oxidation
- Esterification
- Amidation
- Carbamation
- Etherification
- Nucleophilic substitution
- Use of surfactants
- Alternative modifications

DS_{surface} (Degree of Substitution on the Surface) is one parameter used to assess the level of modification carried out on nanocellulose by the different modifications. It will link the degree of substitution on the surface and the number of hydroxy groups that have been modified on the surface of nanocrystals.

Later on, I will discuss different composites in *sections: 4.2 and 4.3* taking into account these modifications, linking them with the new properties acquired.

3.6.3.1. Hydrolysis

Normally, the first modification on nanocellulose is hydrolysis. The most common acids utilized are sulfuric acid (H_2SO_4) and hydrochloridric acid (HCl). Acid choice affects the properties of the final nanocellulose obtained. When using sulfuric or phosphoric acid, nanocellulose surface has negative charge because of the introduction of sulphates and

²³ Eyley S; Thielemans W). Surface modification of cellulose nanocrystals; *Nanoscale*,**2014**, 6, p 7764
DOI: <https://doi.org/10.1039/C4NR01756K>

phosphates. However, these groups can be eliminated by washing them with dilute sodium hydroxide solutions or high temperature.

Undoubtedly, the presence of these groups is an important consideration in the structure and reactivity of nanocellulose surface. Also, the contaminants on the particles need to be considered in the surface modification. It was found that Soxhlet extraction with ethanol of nanocellulose produced by sulfuric acid hydrolysis as a pre-treatment, removed a great number of species from the surface including xylobiose, 1,6-anhydroglucose, vanillin acid and 3,4,5-trimethoxyphenol. The Degree of Substitution on the Surface was $DS_{\text{surface}}=0.16-0.19$.

3.6.3.2. Oxidation

This reaction is performed to introduce carboxylic acid or aldehyde functionalities. There are two common methods: using nitroxyl to produce carboxylic acids selectivity at primary alcohols and periodate oxidation to produce aldehydes from vicinal diols.

TEMPO oxidation is also well known as nanocellulose surface modification. Generally, it is carried out with a catalytic amount of TEMPO with secondary oxidant like sodium hypochlorite or sodium chlorite to recycle TEMPO (*Figure 16 a*)²³).

Optimum pH to perform this reaction is between 9 and 11, it shows good selectivity in primary alcohols. TEMPO oxidation has been applied to nanocellulose using HCl hydrolysis to give negative charge to the surface and to increase stability of aqueous suspensions (*Figure 16 b*)²³).

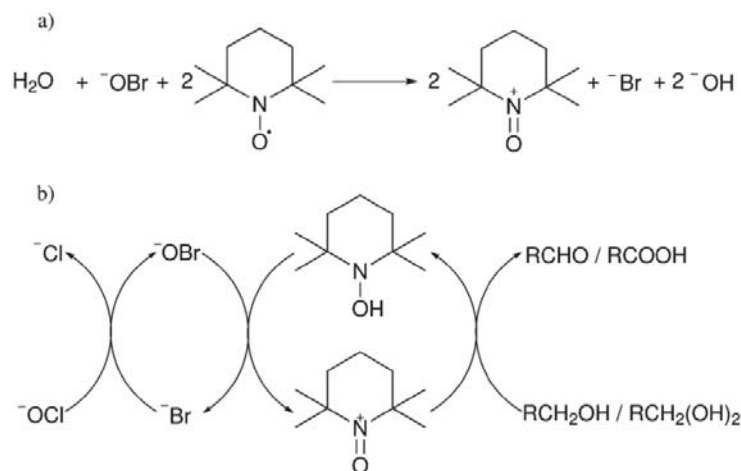


Figure 16: a) Initial formation of oxidant from TEMPO radical b) catalytic cycle of TEMPO using sodium hypochlorite and sodium bromide.

TEMPO oxidation is also used as a precursor to further functionalization of nanocellulose surface.

Other oxidations can be discussed, like periodate oxidation by selective cleavage of vicinal diols, 2,3-diol in cellulose. It consists of breaking the glucopyranose ring of nanocellulose and forming two aldehyde functionalities. It is carried by suspension of nanocellulose sample in NaIO_4 solution (Figure 17²³). Periodate ion coordinates the diol and forms a cyclic intermediate which converts into a dialdehyde, and iodate is lost.

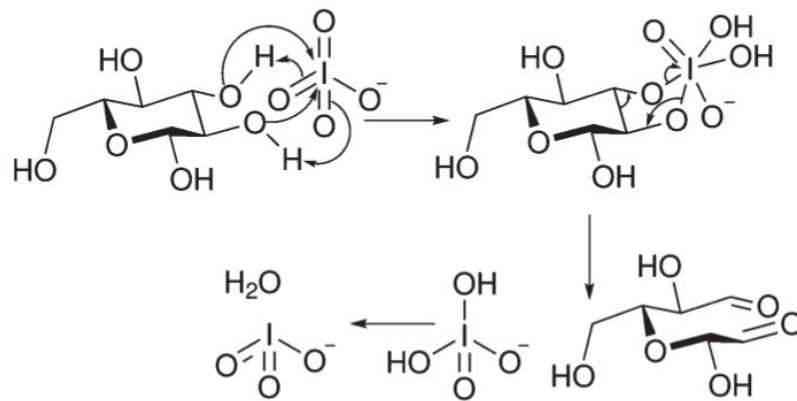


Figure 17: Mechanism of periodate oxidation of cyclic 2,3-diols

Unfortunately, iodate oxidation affects the crystallinity of nanocellulose. Interestingly, TEMPO, chlorine and periodate oxidations are combined to isolate micro and nanocrystalline cellulose with oxidized surfaces.

3.6.3.3. Esterification

Sulfonation and phosphorylation are examples of esterification reactions that occur during nanocellulose hydrolysis. It is stand that almost all the hydroxyl surface is converted to esters. Considering the surface structure, the substitution will create some damage to the crystallinity of the sample due to the reduction of hydrogen bonds. The study claims a degree of substitution $\text{DS}_{\text{surface}}=1,5$. This will result in a significant reduction of the interchain hydrogen bonding network as the most reactive hydroxyl groups in C_2 and C_6 (cellulose structure in section: 3.1) are the ones involved in interchain hydrogen bonds. Acetylation of nanocellulose can also be performed with acetic anhydric pyridine. Pyridine acts as a solvent and forms a driving intermediate for the reaction. The reaction can be seen in Figure 18²³.

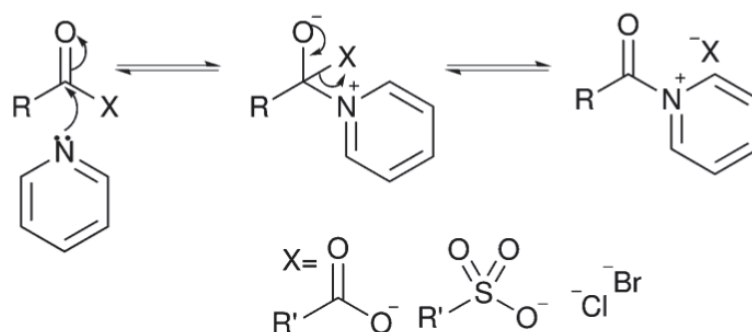


Figure 18: Activation mechanism of anhydrides by reaction with pyridine to form acyl pyridium intermediate.

Transesterification has also been used in the modification of cellulose particles. The methodology consists of modifying nanocellulose with poly(ϵ -caprolactone) or poly(lactide) by ring-opening polymerization. Both mechanisms are represented in Figure 19²³. Normally, the reaction is catalysed by tin (II) 2-ethylhexanoate. However, acid catalysis was also studied.

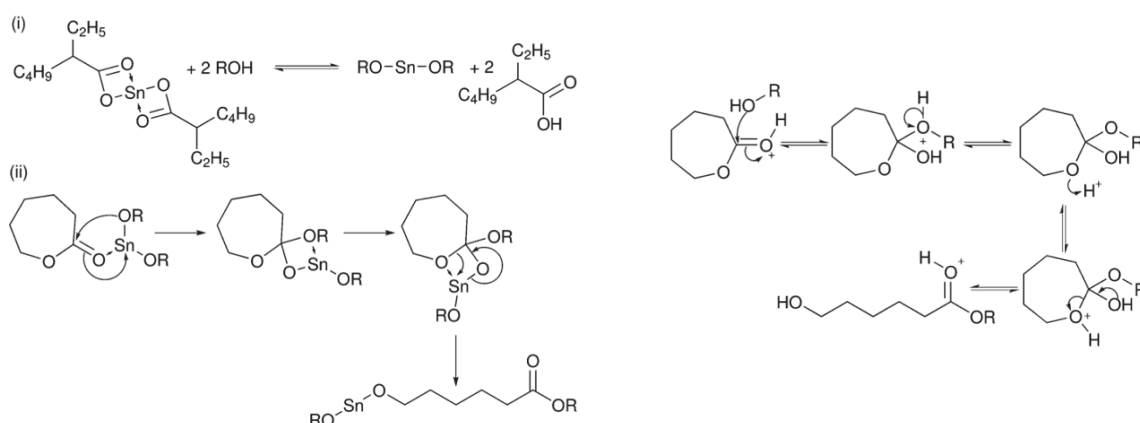


Figure 19: Transesterification mechanism of ϵ -caprolactone catalyzed by tin (II) 2-ethylhexanoate and acid catalyzed mechanism using ϵ -caprolactone.

More recently, acetylation has been performed by transesterification of vinyl acetate in DMF. Cellulose crystallinity in function of the acetylation time was studied. It was found that the structure of cellulose was affected only after 1h of acetylation. Cellulose is partially acetylated to modify its physical properties while preserving the microfibrillar morphology. The degree of acetylation has a huge impact on material properties. In fact, it improves the transparency, reduce hygroscopicity of the composite and improve the thermal degradation resistance of its fibres. Nevertheless, an excessive acetylation reduces their properties.

Regarding all esterification methods, the most common one is the treatment of nanocellulose with acid halide reagents. Bromoisobutyryl bromide (BiB) is widely used.

It makes it suitable for Atom Transfer Radical Polymerization (ATRP). Surface substitution is relatively low, $DS_{\text{surface}}=0.06$. This substituted nanocellulose is used to perform ATRP to obtain fibres grafted with polystyrene and poly-6-[4-(4methoxyphenylazo) phenoxy] hexyl methacrylate.

3.6.3.4. Amidation

TEMPO oxidized nanocellulose is the most common starting material with the objective of amidation of nanocellulose. It consists of activation of the carboxylic acid fraction through formation of N-hydroxysuccinimidyl ester, followed by a reaction with a primary amine to form the amide product (Figure 20²³).

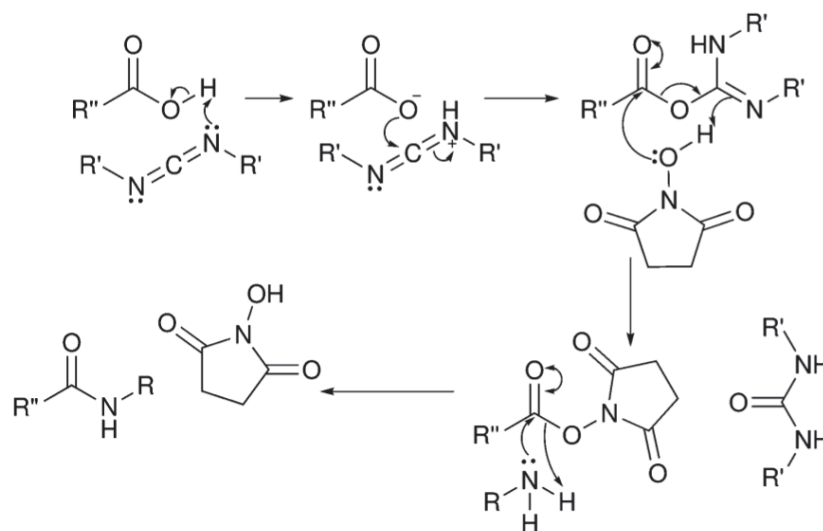


Figure 20: Amidation mechanism using carbodiimides to form an N-hydroxysuccinimidyl ester intermediate.

The reaction is carried in C₆ position, due to the regioselectivity of the previous oxidation. Some authors use different amides and amines to process the reaction, and the DS_{surface} obtained were between 0.12 and 0.17.

3.6.3.5. Carbamation

Modification of nanocellulose by isocyanates can be classified in two groups, represented in Figure 21²³:

- Use of tolylene-2,4-diisocyanate (TDI) to attach functional polymers or other molecules.
- Use of non-polar isocyanates to change the surface properties of the nanocellulose.

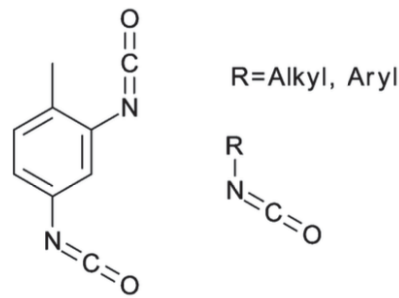


Figure 21: Isocyanates used in the modification of cellulose particles.

First reaction is performed in toluene with triethylamine as a catalyst and reacting 7 days at 90°C. In the reaction, the polycaprolactone (PCL) was first end capped with the phenyl isocyanate at one end. Then reacted in 1:1 stoichiometry with TDI to form mono isocyanate which was subsequently reacted with cellulose to avoid cross-linking between particles. Using toluene, the reaction is limited to the surface of nanocellulose.

3.6.3.6. Etherification

This reaction may have the more extended methodology. The most common etherification of nanocellulose is the application of glycidyltrimethylammonium chloride (GTMAC) or derivatives to cationize the surface of the cellulose. The glycidyltrimethylammonium chloride is added to a suspension of cellulose in 1,75 M sodium hydroxide medium and it is heated for hours. The resulting substitution degree is $DS_{\text{surface}}=0,1$. Using NMR, it is observed a preference in O₆ and O₂ (substitution rather than O₃ (cellulose structure in *section: 3.1*)).

Epichlorohydrin is an epoxide reagent used under similar reaction conditions to modify nanocellulose. They first react with epichlorohydrin in sodium hydroxide solution, followed by ammonium hydroxide reaction to yield primary amine in the surface. This reacts with fluorescein isothiocyanate (FTIC) to give a surface substitution of $DS_{\text{surface}}=0.01$. UV-vis spectroscopy is used to assess the surface modification.

Silylation of cellulose nanocrystals is another type of etherification reported, using alkyldimethylsilyl chlorides of different chain lengths with imidazole in toluene. The silylation occurs rapidly in the first hours, reaching $DS_{\text{surface}} < 1$. Nanocellulose maintain the morphology under mild silylation conditions and could be dispersed into organic solvents. However, if the conditions are too harsh, partial solubilization and loss of fibres structure could occur.

3.6.3.7. Nucleophilic substitutions

All the previous reactions carried out by the authors of the consulted bibliography, involve nanocellulose hydroxyl groups acting as nucleophiles. Performing nucleophilic substitution reactions at nanocellulose carbons open a wide range of functionalization options. The most obvious position for nucleophilic substitution due to steric reasons is C₆, where the primary hydroxyl group is placed. The reaction will occur via S_N2 mechanism. Substitution at secondary positions, C₂ and C₃ (cellulose structure in *section: 3.1*) has been carried out using azide or fluoride as nucleophiles.

A study on the homogeneous azidation of nanocellulose, which is partially tosylated, shows azide substitution in primary and secondary locations, while propionylation of the remaining hydroxyl groups before the substitution reaction leads to limitation of azide substitution to the primary group. It is assumed that the substitution goes through a cyclic intermediate. This fact points that nanocellulose can form epoxides when heating with a base.

3.6.3.8. Surfactants²⁴

In addition, nanocellulose surface can be modified by dispersing agents like surfactants. They are usually amphiphilic organic compounds, and normally present low molecular weight. They contain both hydrophobic groups (tails) and hydrophilic groups (heads). Their use will mean a considerably decrease of dispersive surface energy, thus better nanocellulose phase dispersion on polymers. Mainly, surfactants can be divided in 4 groups: non-ionic, anionic, cationic and amphoteric. This classification depends on the polarity of the head group.

Non-ionic surfactants have no charge groups in its head. Anionic surfactants contain anionic functional groups at their head. They are sulfonate, phosphate, sulphate and carboxylates. Cationic surfactants have positively charged head, like quaternary ammonium cations. Lastly, Zwitterionic (amphoteric) surfactants have both cationic and anionic centres in the same molecule. The anionic part includes sulfonates, and cationic part includes quaternary ammonium cations or amines. The following *Figure 22*²⁵, shows the four kind of surfactants and their polar groups.

²⁴ Prospector®: Surface Active Agents (Surfactants); <https://knowledge.ulprospector.com/3106/pc-surface-active-agents-surfactants/> (accessed: May 19, 2020)

²⁵ Image from source: <http://www.inkline.gr/inkjet/newtech/tech/dispersion/> (accessed: May 19, 2020)

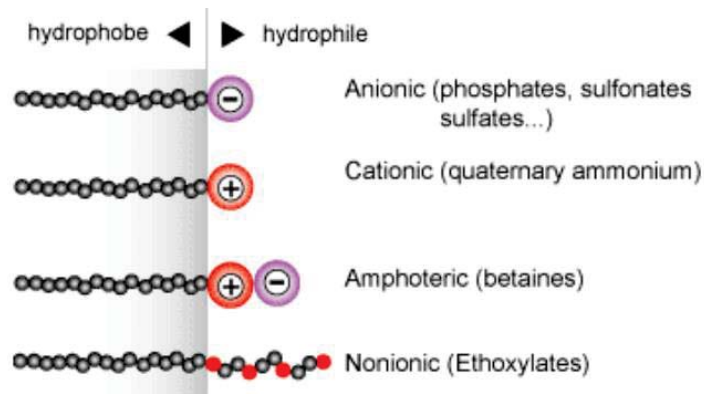


Figure 22: Representation of surfactant types, and their corresponding polar groups.

3.6.3.9. Alternative modifications

All the previously explained reactions have been carried out with unmodified nanocellulose. However, most of them are used as precursors of these reactions shown in Figure 23²⁶.

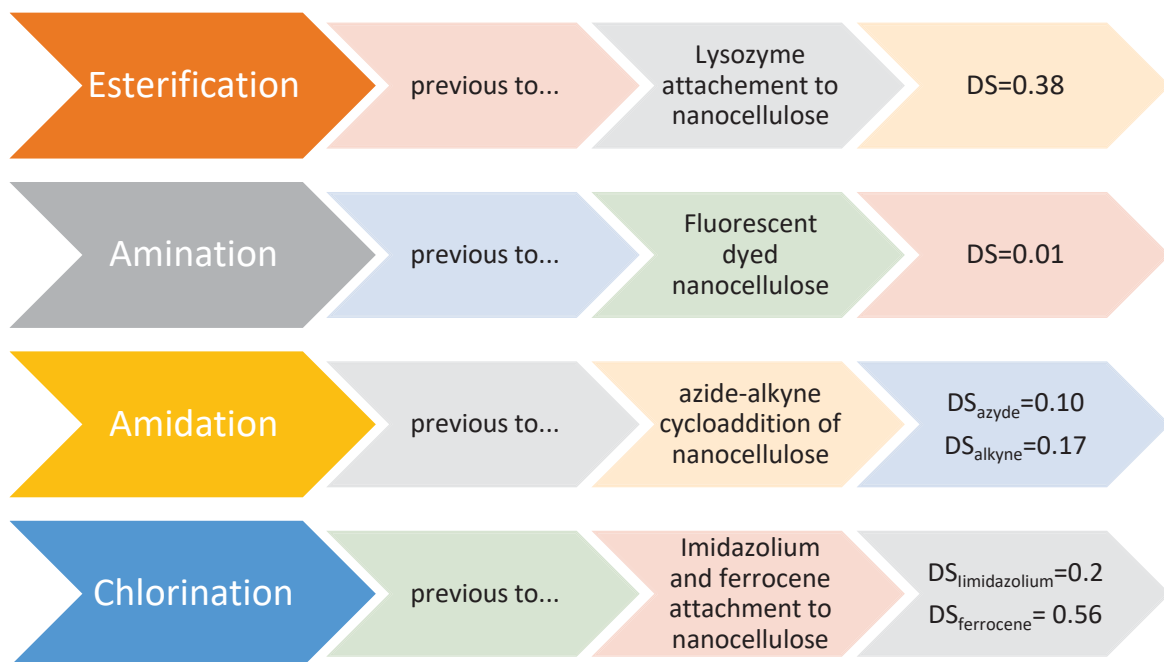


Figure 23: Further reactions with cellulose particles.

As it can be seen, the level of azidation in the ferrocene grafting after chlorination has the higher primary hydroxy groups modification on particles surface, which is unlikely for the nucleophilic substitution involved.

²⁶ Own elaboration adapted from: Eyley S; Thielemans W). Surface modification of cellulose nanocrystals; *Nanoscale*, 2014, 6, p 7764 DOI: <https://doi.org/10.1039/C4NR01756K>

Regarding all the information about nanocellulose modifications, CETIM mainly use hydrolysis, TEMPO oxidation and silylation (type of etherification). Although they have not the highest DS_{surface} , they are simple and feasible reactions. The main objective of nanocellulose modification in this project is to enhance compatibility with the polymers and get an improved material. They are not time consuming, and the nanocellulose modified is stable along the time. Both reactions meet the requirements for achieving the properties that will be explained in *section: 3.7*.

Overall, these modifications let us obtain materials with any desire property. This is the main reason why nanocellulose is used, its versatility. Due to all the possible treatments, it can be widely used in many fields.

3.7. Useful properties of nanocellulose in composites^{27 28}

In all the bibliography research, the nanocellulose particles display high stiffness, even if the amount is less than 5% in the overall composite, the resistance is remarkable. The main properties that are going to be improved or modified in the final composites by adding nanocellulose are: mechanical, thermal and barrier ones.

3.7.1. Mechanical properties

If nanocellulose is well dispersed within the polymeric matrix, improved mechanical properties are expected. Tensile properties of the polymer will increase, that is, the load a material can handle until deformation or break. These properties include tensile strength (tenacity), tensile modulus and ultimate tensile strain. It is remarkable that nanocellulose molecular mass can play an important role in mechanical properties of composites. Varying the mass of nanocellulose, tensile strength increases. In the case of particle-reinforced composites, the particles mostly provide the composite strength.

3.7.2. Thermal properties^{29 30}

Collecting information about thermal analysis of nanocellulose composites with different polymers, I notice that thermal stability of overall composite is improved. Thermal stability

²⁷ (Dima S.O; Panaitescu D.M; Orban C; Ghiurea M; Doncea S.M; Fierascu R.C; Lavinia C; Alexandrescu E; Nicolae C.A; Trică B; Moraru A; Oancea F.) Bacterial Nanocellulose from Side-Streams of Kombucha Beverages Production; *Polymers* **2017**,9, p 374. DOI: <https://dx.doi.org/10.3390%2Fpolym9080374>

²⁸ (K. Van de Velde, P. Kiekens) Biopolymers: overall of properties and consequences on their applications; *Polymer Testing*; 2002; 21 p. 433-442. DOI: [https://doi.org/10.1016/S0142-9418\(01\)00107-6](https://doi.org/10.1016/S0142-9418(01)00107-6)

²⁹ (Nataša Z.Tomić) Thermal studies of compatibilized polymer blends; *Compatibilization of Polymer Blends; Chapter 7*; **2020**; p.489-510. DOI: <https://doi.org/10.1016/B978-0-12-816006-0.00017-7>

³⁰ (Arief C.Wibowo, Manjusri Misra, Hwan-Man Park, Lawrence T.Drzal, Richard Schaleka, Amar K.Mohanty) Biodegradable nanocomposites from cellulose acetate: Mechanical, morphological, and thermal properties; *Compos. Pt. A-Appl. Sci, Manuf.*;37 (9) **2006**; p.1428-1433. DOI: <https://doi.org/10.1016/j.compositesa.2005.06.019>

is the ability of a material to withstand the action of heat and to maintain its properties and chemical composition at a given temperature. Thermal evaluation is normally done with differential scanning calorimetry or thermogravimetric analysis. In general terms, the stronger the inter and intramolecular hydrogen bonds between cellulose and the polymer, the higher the temperature range the composite will handle.

Also, the amount of nanocellulose in the composite has an influence on the thermal stability. As cellulose acts as a reinforcement, the higher the content the higher stability.

3.7.3. Barrier properties¹⁹

Finally, barrier properties development will lead to efficient materials for many applications. They are constituted by water vapor transfer rate (WVTR), water permeability (WVP), oxygen transmission rate (OTR) and oxygen permeability. The main objective is the increment of all of them.

The WVTR is referred to the water vapor that can pass through a composite per unit area and time under specific conditions. Different types and modifications of nanocellulose will influence these barrier properties. The reduction of cellulose from macro to nano scale results in a decrease in WVTR. The physical structure of micro or nanocellulose have an impact on the permeability of composites.

The degree of cellulose crystallinity influences the barrier properties. Micro cellulose present large amorphous structure compared to nanocellulose. Thus, nanocellulose composites, due to their more organized and crystalline structure, will provide a barrier to water.

Nanocellulose modifications also improves WVTR. The oxygen barrier prevents from oxidation though oxygen in the surrounds of a material. Humidity and crystallinity of the nanocellulose are related with the OTR. An increase of humidity is attributed to crystalline structure of cellulose to form hydrogen bonds with oxygen, so increase the permeability.

4. Polymers: Matrix phase⁶

The matrix phase in the composites treated in this work is **polymeric**. In a broad sense, a polymer is a material consisting of very large molecules, or macromolecules, composed of many repeat subunits, as shown in *Figure 24*⁶. The term **monomer** refers to the small molecule from which a polymer is synthesized (hence monomer and repeat unit mean different things). Within each macromolecule, the atoms are bound together by covalent interatomic bonds. Most of polymers of industrial interest are organic, being the backbone of each chain a string of carbon atoms.

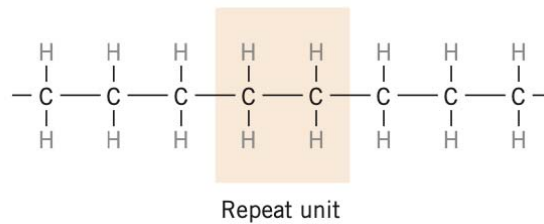


Figure 24: Schematic representation of repeat unit and chain structure of a polymer molecule.

The physical characteristics of a polymer depend not only on its molecular weight and shape but also on differences in the structure of the molecular chains.

Regarding molecular structure, polymers can be classified as linear, branched, cross-linked and networked. In linear and branched polymers there may be van der Waals and hydrogen bonds between the chains. However, in cross-linked ones, adjacent linear chains are bonded one to another at some positions by covalent bonds. Finally, in network polymers, multifunctional monomers forming three or more active covalent bonds make three-dimensional networks. In *Figure 25*⁶ this polymer classification can be seen.

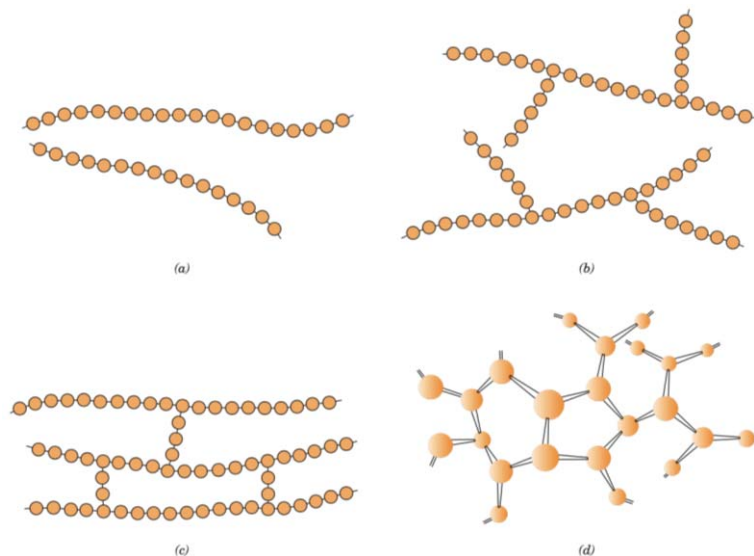


Figure 25: Schematic representation of (a) linear, (b) branched, (c) crosslinked, and (d) network (three-dimensional) molecular structures. Circles represent individual repeat units.

Another classification of polymers, closely related to the previous one, is the one made according to behaviour with rising temperature, in **thermoplastics, thermosets and elastomers** I'm going to comment the main properties³¹ of these polymers and why thermoplastics will be used as main matrix in composites for his project.

Thermoplastics: they can be pictured as a mass of intertwined chains. The binding forces are covalent bonds between molecules (inside the chains) and Van der Waals forces between chains.

They can melt when heating and became hard when cooling. Both characteristics are reversible, and they can be reheated and reshaped repeatedly. Their structure can be crystalline, partially crystalline or amorphous. Thermoplastics at ambient temperature have great rigidity, hardness, and solvent resistance. A wide range of common compounds belong to thermoplastics:

Polyethylene (PE)	Polycarbonate (PC)
Polypropylene (PP)	Polymethyl methacrylate (PMMA)
Polyvinyl chloride (PVC)	Polyamides (PA)
Polystyrene (PS)	Etc.

Thermosets: their chains are bonded together by covalent bonds; thus, the thermosets are more rigid than thermoplastics, and in general they have higher strength.

They create three dimensional networks when they are heated. After they are formed, they cannot re-melt neither reformed. There are many examples:

Polyurethane (PUR)	Silicone
Unsaturated polyesters	Phenol (formaldehyde resins)
Epoxy resins	Urea (formaldehyde resins)
Vinyl resins	Etc.

Elastomers materials are rubberlike polymers with T_g (glass temperature: temperature over which gradual and reversible transition in amorphous materials, from a hard and brittle "glassy" state into a rubbery state is produced as the temperature is increased.) below room temperature. They can also be stretched beyond their original length and can retract rapidly to their original dimensions. Elastomers are flexible and present chemical resistance. Examples: styrene and acrylonitrile.

³¹(Edward N. Peters; Carl Zweben) ``Handbook of Materials Section``; **2002**; (chapters 11,12), p.335-399.
DOI: <https://doi.org/10.1002/9780470172551.ch12>

Thermoplastics are the polymers selected for this research, and the ones used in CETIM project composites, due to their appealing properties.

Thermoplastics³² are the polymers chosen, not only because of their world production (*section: 1.1*), but also because they show interesting properties. Their structure make possible the use of many processing composite techniques. In addition, they can be reshaped by heating and then cooling by various processing techniques like extrusion or injection molding.

The recent interest in total biodegradable composites, focuses the attention in the use of biodegradable thermoplastic matrices: **biopolymers**. They improve physical and mechanical properties of the composites. However, they present limiting aspects regarding density and temperature. Polylactic acid or polylactide (PLA), polyglycolic acid or polyglycolide (PGA) and polyhydroxy butyrate (PHB) are some examples of biopolymers that are going to be used in CETIM project; **Error! Marcador no definido..**

Thermoplastics are usually fossil-based materials, from natural gas, coal, mineral or oil. However, they can be also bio-based materials produced from renewable carbon resources. These **bio-based polymers**^{Bio-based} polymers will be used as another type of matrix. They are considered eco-friendly materials. However not all of them are biodegradable. For example, bio-PE is synthesized from bioethanol, but it is not biodegradable. Also, bio-PET is produced from biomass using bio-based ethylene glycol. These polymers are going to be explained in *section: 4.4*.

4.1. Polymer modifications³³

Although nanocellulose modification is commonly used to achieve compatibility between both phases in nanocomposites, matrix can also be modified. As I commented in *section: 1.1*, thermoplastics have hydrophobic nature. Fortunately, they can be modified to improve properties like tensile strength or wettability of the overall composite. In addition, some processing techniques that were restricted for net polymers can be used.

Polymer surface modifications are mainly based on grafting methods. Grafting can proceed through `grafting from` and `grafting onto` mechanisms. The first is used with

³² (Tibor Alpár, Gábor Markó and László Koroknai) Handbook of Composites from Renewable Materials; **2017**; (12) p. 287-295. DOI: 10.1002/978111944163

³³ (Thi-Thu-Loan Doan, Shang-Lin Gao, Edith Mäder) Jute/polypropylene composites: Effect of matrix modification; *Compos. Sci. Technol.*; **2006**; 66, p.952-963. DOI:<https://doi.org/10.1016/j.compscitech.2005.08.009>

ring opening polymerization (ROP), ATRP and single-electron transfer living radical polymerization (SET-LP). In the second one, different coupling agents are used, such as maleic anhydride.

In addition, compatibilizing agents can also be used as a polymer modification.

4.1.1. Grafting methods³⁴

This modification is used for the incorporation of properties like hydrophilicity, hydrophobicity and resistance towards acid-base attack with higher thermal stability. Parameters like melting point, glass transition temperature, solubility, permeability, chemical reactivity and elasticity of the polymer can be modified through grafting methods. Basically, it consists of a polymeric backbone where functional groups are covalently attached.

4.1.1.1. `Grafting from` method

`Grafting from` involves the generation of active sites on the polymer which starts the monomer polymerisation onto polymer backbone and as a result, a graft copolymer is formed. This is a polymer in which the repeating units are two different monomers.

This method provides a technique that incorporates dyeing ability, crease resistance, moisture and chemical resistance in the backbone polymer. The main principle of graft copolymerisation is the generation of active sites, in the form of free radicals or functional groups. ATRP generates free radicals by capping halogen atoms onto inactive sites, which are transferred to metal complexes in lower states. In addition, graft copolymerization can involve radiation as an initiation system.

4.1.1.2. `Grafting onto` method

`Grafting onto` is based on chemical methods. They involve the use of coupling agents as initiators of active sites. Mainly they are Lewis acids, strong bases and metal carbonyls such as: anhydrides, maleate polymers, isocyanates and alkoxy silanes.

Among all the commercial coupling agents, **maleic anhydride** used in thermoplastics has been found to be the most efficient interfacial adhesion improvement for composites of cellulose particles. Undoubtedly, there are many factors that affects mechanical properties: moisture disperse phase type, matrix/fibres interface, temperature and humidity.

³⁴ (Susheel Kalia, Magdy Wadid, Sabaa Sarita Kango) Polymer grafting; Polysaccharide based graft copolymers; **2013**; p.1-14 DOI: https://doi.org/10.1007/978-3-642-36566-9_1

4.1.2. Compatibilizing agents³⁵

Poor interfacial adhesion between the phases of composites can be solved using compatibilizing agents. They became chemically linked to the hydrophobic part of nanocellulose, facilitating the wetting of the hydrophobic polymer chain. In other words, they provide both characteristics, hydrophilicity and hydrophobicity, thus the adherence will be optimized.

Regarding the effect over tensile properties, the addition of these agents will significantly improve tensile strength to the same level than pure thermoplastics. The mechanism of compatibilizing agents are showed in *Figure 26*³⁵.

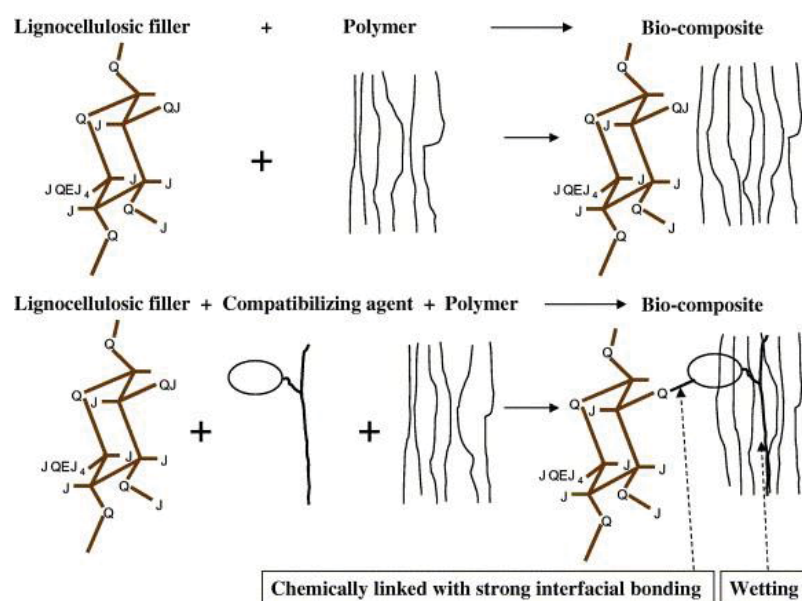


Figure 26: Compatibilizing agent roll in matrix/fibres surface.

4.1.2.1. Polyethylene-co-vinyl acetate (EVA)³⁶

One attractive compatibilizer agent is polyethylene-co-vinyl acetate (EVA). EVA is a polar copolymer where the amount of vinyl acetate (VA) can vary, changing its polarity. The presence of polar groups makes EVA an ideal modifier for organic compounds, not only polymers. The efficiency of EVA will depend on the compatibilization on the phases and the amount of VA. Some thermoplastics like low density polyethylene (LDPE), in combination with this agent show attractive properties in composites: low cost, low

³⁵ (Han-Seung Yang, Hyun-Joong Kim, Hee-Jun Park, Bum-Jae Lee, Taek-SungHwang) Effect of compatibilizing agents on rice-husk flour reinforced polypropylene composites; *Compos.Struct*; **2007**; 77, p.45-55. DOI: <https://doi.org/10.1016/j.compstruct.2005.06.005>

³⁶ (F.P La Mantia, S. Lo Verso, N Tzankova Dintcheva) EVA copolymer based nanocomposites; *Macromol.Mater. Eng*; **2003**; 287, issue 12. DOI: <https://doi.org/10.1002/mame.200290019>

density and versatility. However, mechanical properties such as rigidity are quite low. This is the reason why it is not often used.

When preparing nanocomposites, if the matrix is an apolar polymer, it is difficult to intercalate single layers of the dispersed phase among the matrix. EVA has been proved to enable the dispersion of the polar fillers, and no additional compatibilizer is needed.

A bibliographic research of composites formed by cellulose derivatives and different polymers will be exposed in the following section. The classification goes from convectional polymers to biopolymers. The previous information described, composite processing techniques, cellulose pre-treatments and isolation processes, cellulose types and nanocellulose and polymers modifications were for the understating of this section, where all the concepts are taken into account.

Composites properties are explained. Later, in *section: 5.1*, an overall collection of the information described here is placed in a table, seeing the main facts.

4.2. Modified thermoplastics⁶

Nanocellulose incorporation in convectional thermoplastics such as polystyrene (PS), polyethylene (PE) and polypropylene (PP), reinforces and makes these polymeric systems richer in renewable material composition.

Figure 27 shows the different repeat units of the main convectional polymers that are going to be considered in the present project.

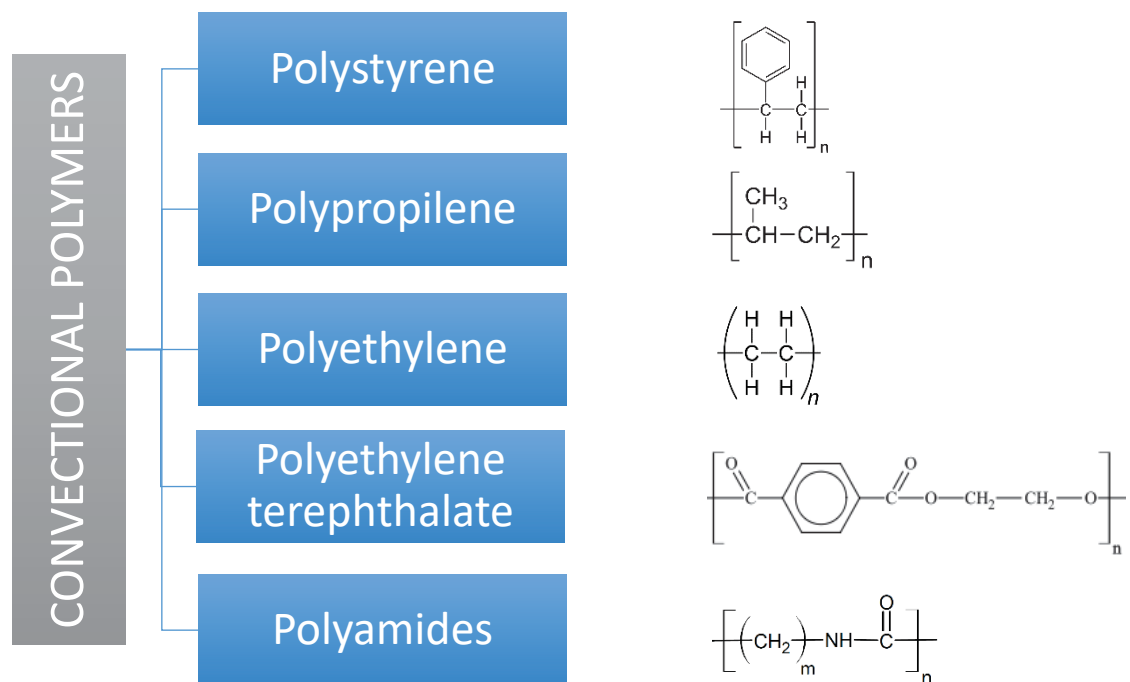


Figure 27: Main convectional polymers studied in the project and their repeat unit.

4.2.1. Polystyrene⁶

The first thermoplastic that is considered is polystyrene (PS). As a pure polymer it shows great characteristics, excellent electrical properties and optical clarity, good thermal and dimensional stability and it is relatively cheap

- Some of its applications are wall tiles, battery cases, toys, indoor lighting panels and appliance housings etc.

It can be combined with the different nanocelluloses types described in *section: 3.5*. Their treatments and modifications (*sections: 3.6.1 and 3.6.3*) and composites improved properties are also described here:

- **CNFs**¹⁶: regarding its chemical treatment, oxidation by TEMPO using DMF as solvent is reported. Homogeneous dispersion of the fibrils into polymeric matrix is enabled. In addition, an improvement in tensile strength and elastic modulus of the PS is achieved in the composites.
- **Nanocellulose whiskers**³⁷: templating process (composite fabrication method) is applied to prepare composites of immiscible components. Firstly, nanocellulose is formed by sol/gel process. A homogeneous aqueous dispersion is formed, followed by gelation through solvent exchange with water-miscible solvent.
For a successful template approach, the polymer solvent must be miscible with the gel solvent and not re-disperse the nanocellulose. Polystyrene/cellulose whiskers composites are prepared with a content of 2.5-16.7% v/v.
- **CNC**³⁸: these crystals are prepared by acid hydrolysis from native cotton fibres. Laboratory milling is used as isolation technique to obtain fine particles. Then, an acid hydrolysis is performed at 45°C with 65% wt of H₂SO₄ for 45 minutes stirring. Subsequently, TEMPO oxidation is produced. Composites from CNC reinforced PS matrix are prepared by extrusion. They are introduced in the extruder at 200°C and 150 rpm for 10 minutes.
Above T_g, the reinforcing effect of nanocrystals become apparent and the modulus of the composite is higher than neat PS material. The thermal stability also increased in relation with neat PS.

4.2.2. Polypropylene⁶

This thermoplastic is commonly used in composites formation. In fact, it one of the main polymers used in CETIM project. It presents resistance to heat distortion, excellent electrical properties and fatigue strength. It is chemically inert and cheap.

- It normally uses and applications were described in *section: 1.1*.

³⁷ (P Jitendra K. Pandey, Hyun Taek Lee, Hitoshi Takagi, S. H. Ahn, D. R. Saini, M. Misr) Dispersion of NC in PP and PE matrix; *Handbook of polymer nanocomposites*, **2015**, 56, p.1-10. DOI: https://doi.org/10.1007/978-3-642-45232-1_56

³⁸ (Ning Lin and Alain Dufresne) Physical and/or Chemical Compatibilization of Extruded Cellulose Nanocrystal Reinforced Polystyrene Nanocomposites; *Macromolecules*, **2013**; 46 (14), p.5570-5583. DOI: <https://doi.org/10.1021/ma4010154>

It can also be combined with different nanocellulose types with different modifications and treatments found in the bibliography:

- **Crystalline micro/nanocellulose from wood flour³⁷** (WF): a suspension of micro and nanocellulose is obtained by alkali, acid and mechanical treatment of wood. The matrix is modified through reactive extrusion grafting of maleic anhydride.

Dispersion is better at lower concentrations due to the availability of greater number of functional groups from maleic anhydride-grafted polymer chains in the samples. Mechanical properties also improve at lower filler loadings. All in all, uniform dispersion of cellulose is considered more important than the filler concentration in the polymeric matrix.

- **Cellulose nanowhiskers³⁷** (CNW): composites with this nanocellulose are evaluated for PP matrix. Composites were reported for three types of cellulose as reinforcing phase:
 - Aggregated nanocellulose in toluene
 - Suspension of nanocellulose in water, mixed with a surfactant: phosphoric ester
 - Grafted cellulose with maleated polypropylene

Composites are prepared by solvent casting. Solubilized polypropylene is mixed with hot toluene (110 °C) with each NC dispersed in several toluene concentrations. It can be seen that tensile strength increases. Ductility and elongation can be maintained adding surfactant-coated nanofillers. Overall, mechanical properties are determined on the filler/ filler interactions and in the extent of dispersion along the matrix.

- **NC from soybean³⁷**: the procedure used is a melt-blending method. An acrylic monomer, ethylene-acrylic oligomer emulsion is added. As a result, the interaction between hydroxyl groups of cellulose are reduced. Consequently, particles dispersion in the composite matrix is enhanced. This acrylic oligomer acts like a bridge between hydrophilic and hydrophobic components.

The stress-strain behaviour of this composite's changes, increasing modulus and decreasing elongation. Nanocellulose is uniformly dispersed in the polyethylene matrix.

- **NC³⁷**: extracted by acid hydrolysis. Maleic anhydride grafted polypropylene (MAPP) is employed as compatibilizing phase between nanocellulose and matrix. Both types of PP are dissolved in toluene at 105-110°C. Nanocellulose was added from 0-15% wt, into dissolved MAPP, followed by sonication for 2h to enhance dispersion. MAPP and filler solution are added to dissolved PP. Composites are prepared by solvent casting. Regarding properties, there is a surprising improvement of tensile strength when reinforced composites were noticeable. Crystallinity was also improved.

4.2.3. Polyethylene⁶

Polyethylene (PE) is one of the most used polymers in composites formation along with PP. It presents magnificent properties as polymer: it is chemically resistant and electrically insulator, tough and with a relatively low coefficient of friction. However present low strength and poor resistance to weathering. Although it presents some drawbacks, it has many applications explained in *section: 1.1*.

In some studies, composites of PE were prepared, using Low-Density Polyethylene (LDPE). Polyethylene is a branched polymer, where ramifications can be larger, in the case of High-Density Polyethylene (HDPE) or shorter like in LDPE.

- **Ramie CW³⁹**: in content from 0 to 15% were used unmodified and chemically modified. For the formation of the composites, an extrusion machine with twin-screw is used. The filler is employed in dry state after water or organic solvent evaporation. The components were introduced in the mixing chamber and melt at 160 °C. The mix was set at 60 rpm for 10 min. The modified cellulose, by acid hydrolysis shows elongated nanocrystals with high aspect ratio regarding unmodified cellulose. Regarding mechanical properties, tensile modulus has a drop observed at -40°C due to semi crystalline nature of cellulose. Tensile test was performed at room temperature. Strain-stress curves show a slight decrease of tensile strength and slight increase in tensile modulus upon whiskers addition.

³⁹ (Aparecido Junior de Menezes, Gilberto Siqueira, Antonio A.S. Curvelo, Alain Dufresne) Extrusion and characterization of functionalized cellulose whiskers reinforced polyethylene nanocomposites. *Polymer*, **2009**, 50 p 4552-4563. DOI: <https://doi.org/10.1016/j.polymer.2009.07.038>

4.2.4. Polyethylene terephthalate (PET)⁸

This thermoplastic is one of the most used in textile materials due to its excellent properties of wash-to-wear, chemical resistance, heat stability, high tenacity and resistance to wrinkling. Nevertheless, high crystallinity and lack of polar groups such as -COOH and -OH on main chains, cause a low surface free energy, poor adhesion, static electrification, low wettability and high hydrophobicity. To overcome these problems composites are created. The nanocellulose types used in different investigations are:

- **CNC**⁸: containing hydrophilic surface agents to modify PET and produce coating durability, moisture retention and wettability on PET surface. Consequently, the surface was changed from hydrophobic to hydrophilic after the treatment. Due to the use of cationic CNC agents, the surface shows superior adhesion onto the cationic PET surface in comparison with unmodified CNC.

The use of CNC as a filler in these composites broad the phase change temperature range and improve thermal stability. They are used as effective phase-change materials for insulation or applications that requires durability at high temperatures.

- **CNF**⁸: this nanocellulose type is used in CNF/PET nonwoven composite separator. CNF is modified with polyethylene glycol (PEG) to get immobilized in PET surface. Wet-laid non oven process was used, and the separator achieves optimal properties in wettability, mechanical strength, thermal resistance and electrochemical performance. The composite structure was obtained by coating PET with CNF.

4.2.5. Polyamide⁴⁰

Polyamides (PA) like Nylon are well known due to their characteristics and applications. They present good mechanical strength; abrasion resistance and toughness and they have low coefficient of friction. One drawback when preparing composites is the fact that they absorb water and some other liquids.

- They are mainly used in bearings, gears, cams, bushings, handles and jacketing for wires and cables.

⁴⁰ (Correa A.C; Texeira E; Carmona Brait V; Bruna K; Teodoro R; Ribeiro C; Capparelli Mattoso L.H; Marconcini J.M) Obtaining nanocomposites of polyamide 6 and cellulose whiskers via extrusion and injection molding. *Cellulose*, 2014, 21 p 311-322. DOI: [10.1007/s10570-013-0132-z](https://doi.org/10.1007/s10570-013-0132-z)

Composites with polyamides as matrix are mainly formed with the following nanocellulose type:

- **NCW from cotton fibres**⁴⁰: extrusion or injection molding processes are difficult to use for the addition of this nanocellulose in composites. The reason is the low thermal stability of nanoparticles and the high processing temperature of polyamides, which is higher than thermal degradation of the whiskers.

Consequently, nanocellulose whiskers were coated with polyamide (PA6) to increase thermal stability and avoid agglomerates formation. The coating on nanocellulose whiskers allows their application at relatively high temperatures, around 250°C.

The whiskers were modified by acid hydrolysis. Freeze-dried CWs were coated with PA6 by dispersing them in formic acid and PA6 was solubilized in the suspension. The percentage of CWs used was 1% wt. The results show that agglomeration can be prevented if CWs are coated by PA6 and they present thermal stability from 180-280°C, allowing the use of extrusion or injection molding to form composites.

Regarding PA6+1%CWs composites and neat PA6 without nanocellulose, the specimens increase 45% the elastic modulus when whiskers are present. Also, dispersion among the matrix is improved and thermal stability increase with only 1% of CWs.

4.3. Modified biopolymers⁴¹

Thermoplastics have some environmental drawbacks. First, the vast majority are made from non-renewable fossil fuels. Secondly, they are supposed to be inertness to chemicals, microorganisms and light, that make them difficult to dispose of in an eco-friendly way. There are already several solutions, one of them is the use of degradable polymers from renewable resources such as poly (hydroxyalkanoates) or starch among others (Figure 28). They will be discussed in this section. In addition, the incorporation of nanocellulose in biopolymers is an efficient strategy to obtain properties of convectional polymeric materials.

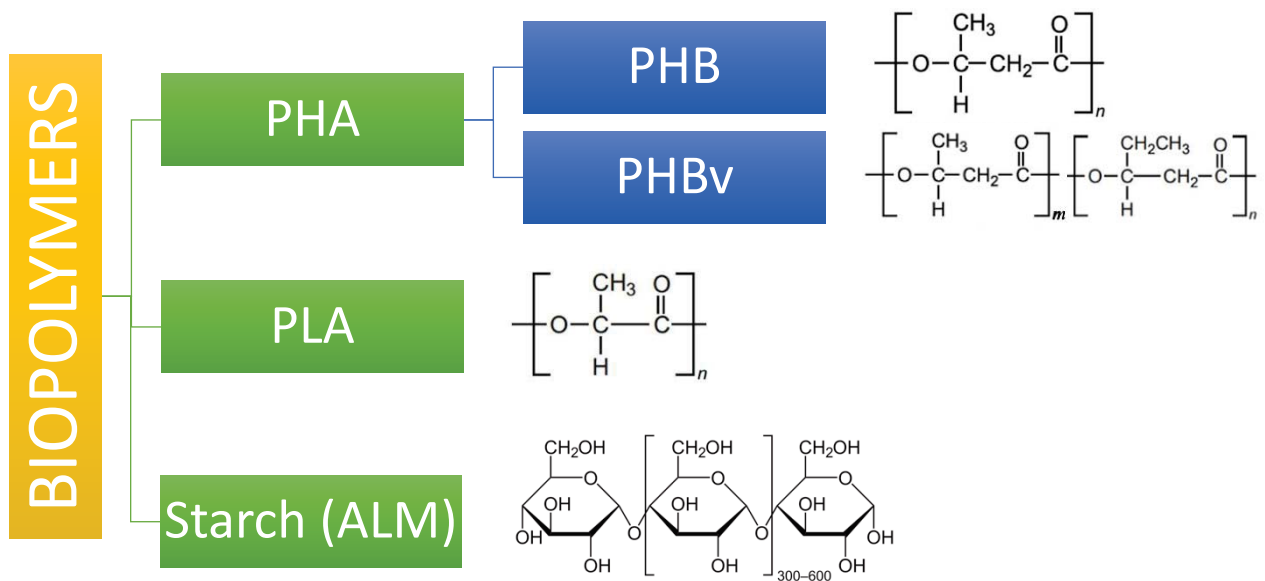


Figure 28: Different types of biopolymers and their repeat units.

4.3.1. Poly (hydroxyalkanoate) PHA

PHAs are now much used. They come from renewable materials and are readily degradable. PHAs are bio polyesters that can be produced by a wide variety of bacteria.

Figure 29⁴¹ represent the general formula for PHAs.

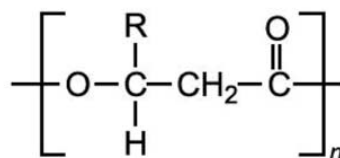


Figure 29: repeat unit of any kind of PHA

⁴¹ The Essential Chemical Industry- online;
<https://www.essentialchemicalindustry.org/polymers/degradable-plastics.html> (Visit data: 27/05/ 2020)

4.3.1.1. Poly (hydroxybutyrate) PHB⁴²

Within the range of these materials, the homopolymer poly (hydroxybutyrate) (PHB) is the best known. It is produced by bacterial fermentation of glucose solutions (produced by starch in hydrolysis). It has been studied due to its appealing characteristics; it presents mechanical properties similar to conventional petroleum-based polymers. It also possesses a relatively high crystallinity. However, it is excessively brittle and has low thermal stability, which makes it unstable during melting processes.

To overcome these problems, there are several solutions. Firstly, PHB can be blended with poly (vinyl alcohol) (PVA), or poly (ethylene oxide) (PEO). Secondly, modifiers/plasticizers by copolymerization can be added. Copolymers such as hydroxybutyrate (HB) with hydroxyvalerate (HV) will produce poly (3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV). Increasing the content of HV, melting temperature is reduced without reducing the thermal stability of the material. Tributyrin (TB) and poly(adipatediethylene) (A) among others, are commonly employed too. The use of plasticizers overcome the drawback of PHB and improve mechanical characteristics like ductility, impact strength and deformability. However, PHB polyester can be used without modification in some composites. The types of nanocellulose utilized are:

- **CNC**⁴²: in this case composites are produced by solvent casting. Nanocellulose is obtained as a suspension in dimethylformaldehyde (DMF), on amounts from 2% wt. to 4% wt. After being sonicated for 30 minutes, the nanocellulose suspension is added to PHB solution in DMF too. The mixture is again sonicated for 10 minutes.

These composites present higher thermal stability compared with neat PHB, confirming the interaction between CNC and matrix. This kind of nanocellulose reduce the hydrophobic character of the final sample, as a consequence, the dispersion in matrix is poor.

- **BNC**⁴² is also used. The process is the same as with CNC. The only difference is that instead of sonication, BNC is homogenized two times for 15 minutes each time. In addition, when mixing both solutions, they are again homogenized for 10 minutes. Thermal stability of BNC composites is reduced.

Plasticized PHB samples are prepared by adding 20% wt of plasticizer like TB or A, to a PHB solution. When they are used in composites, degradation temperature is reduced.

⁴²(Seoane I.T, Mnafredi L.B, Cyras V.P, torre L, Fortunati E, Puglia D) Effect of Cellulose Nanocrystals and Bacterial Cellulose on Disintegrability in Composting Conditions of Plasticized PHB Nanocomposites; *Polymr*, **2017**; 9 (11), p. 561. DOI: <https://doi.org/10.3390/polym9110561>

There is no influence on the melting point when adding plasticizers to the BNC composites. Nevertheless, CNC composites present an increment in the melting temperature, due to the increment of the crystalline order.

Regarding **PHBv**, it is highly studied for food packing industry, biomedical applications and tissue engineering due to its appealing properties: transparency and structural stability, which support cellular growth and proliferation.

However, its applications are limited due its hydrophobic nature, high crystallinity and poor mechanical and thermal properties. Fortunately, the problem can be overcome by creation of composites with nanocellulose. This will enhance thermal and mechanical properties even at low contents of fillers. The nanocellulose acts as a barrier to hinder the absorption of the diffusion of water through the polymer chain. The types of nanocellulose that can be employed are:

- **Bacterial cellulose nanowhiskers**⁴³ (BCNW): it is produced by acid hydrolysis of BC. It presents several advantages over other nanocellulose resources. It is highly pure and crystalline and high aspect ratio. For composites prepared by solution casting with 2,3% wt of this nanocellulose, and up to 5% wt containing 30% wt of PEG as compatibilizer, the mechanical properties are improved.
- **CNC**⁴⁴: composites are prepared by solution casting method. 10% of PHBv is solved in chloroform at room temperature. Then, the mixture is heated at 70°C stirring for 30 minutes. From 3-20% wt. of CNC suspension is added. The mixture is sonicated for 30 minutes.
Compared with neat PHBv, maximum decomposition temperature is increased. Composites decomposed at higher temperatures than neat PHBv. Besides, hydrogen bonding interaction between the hydroxyl groups of CNC and ester carbonyl groups of PHBV are helpful to improve the degradation temperature.

⁴³(Marta Martínez-Sanz, Marianna Villano, Catarina Oliveira, Maria G.E.Albuquerque, Mauro Majone Maria Reis, Amparo Lopez-Rubio, Jose M.Lagaron) Characterization of polyhydroxyalkanoates synthesized from microbial mixed cultures and of their nano biocomposites with bacterial cellulose nanowhisker; *New Biotechnology*; **2014**; 31, P.364-376. DOI: <https://doi.org/10.1016/j.nbt.2013.06.003>

⁴⁴(Somia Yassin Hussain Abdalkarim, Hou-YongYu, Mei-Li SongYing Zhou, Juming Yao, Qing-Qing Ni) In vitro degradation and hydrolytic mechanisms of PHBV nanocomposites; *Carbohydr Polymr*; **2017**, 176, p.38-49. DOI: <https://doi.org/10.1016/j.carbpol.2017.08.051>

4.3.2. Polylactic acid (PLA)⁴⁵

Another degradable polyester is poly (2-hydroxypropanoic acid) (polylactic acid, PLA), produced from 2-hydroxypropanoic acid (lactic acid). It can be obtained from renewable sources like corn, potato, cane sugar and rice. Lactic acids from these sources are produced by fermentation process and used as monomer to synthesize PLA through different polymerisation routes: ROP, polycondensation and other direct methods (e.g. enzymatic polymerization). PLA is available with different molecular weights. ROP produce high molecular weight PLA, compared with polycondensation method.

PLA present valuable properties such as biodegradability, UV stability, biocompatibility and renewability. It has good mechanical properties regarding conventional petroleum-based polymers. However, it suffers from some shortcomings like low thermal resistance, heat distortion temperature and slow rate of crystallization. Fortunately, different cellulose fillers can be added to overcome these drawbacks. In addition, PLA can be modified by blending with other polymers and copolymerizing with monomers. The main nanocellulose types that were found in composites of PLA are:

- **CNF⁴⁵** they are combined with PLA microfibrils through injection molding in a proportion of 3% wt. CNF suspension is mixed with PLA fibrils using a homogenizer, followed by sonication to enhance interaction. The mixture is filtered and hot pressed at 100°C. Different temperature and pressures are used with different ratios of composite phase compositions.

It was found that an increase in PLA fibrils content increase opacity of composites. When using modified PLA as matrix, the final composite absorbed 43% less moisture in comparison with unmodified PLA. This may be due to the polymer have few -OH groups available on the surface of CNFs.

- **CNCs⁴⁵** are initially modified by silylation, and it is mixed with PLA by extrusion at 165 °C (100 rpm, 5 min). In comparison with unmodified CNC, after the silylation of CNC the samples remain colourless, which confirm the silane treatment. Also, the modification reduces the thermo-sensibility and allows the dispersion via extrusion. The percentages of cellulose used, vary between 5 and 35% wt.

Using maleic anhydride-grafted PLA, interfacial adhesion between PLA and CNCs improve. The optimal conditions are: “5+10 min” (5 minutes extruding only

⁴⁵(T.C.Mokhena, J.S. Sefadi, E.R. Sadiku, M.J. John, M.J. Mochane, A.Mtibe) Thermoplastic processing of PLA/Cellulose nanomaterials composites. *Polymr.* **2018**; 10 (12) p.1363. DOI: <https://doi.org/10.3390/polym10121363>

PLA, then in minute 5 CNC are added, and both phases are mixed during 10 min), and 190°C temperature for extrusion, to avoid PLA and CNC degradation as well as incomplete dispersion of the fillers. Regarding mechanical properties, tensile strength and elongation are improved. The percentage of nanocellulose used, suppose an improvement in tensile modulus when increasing the amount.

- **BNC**⁴⁶: these composites are created by solvent casting method. PLA was dissolved in dichloromethane at 10% w.t. BC films (with dimension 150x15x5 mm) soaked in dichloromethane, are immersed in PLA solution for 24 h to allow diffusion of PLA through the films. Then, they are retired, dried at room temperature and then dried under vacuum for 24 h.

As the interface between reinforcement and PLA is not optimum due to their polarity differences, BNC fibers are modified with MA. Normally this modification is done to the matrix polymer, however nanocellulose can also be modified with maleic acid.

Tensile properties of the composites are improved in comparison with neat PLA. Also, elongation to break is dramatically lower than pure PLA. Normally, the addition of reinforcements reduces the elongation to break as they stress concentrations and limit the molecular movement of the matrix.

The modification of BNC has an influence on the mechanical properties of the composite. When MA is used, BNC can better swell in dichloromethane, this PLA get more diffused in BNC films. Modified BNC composites have low BNC content, 6% w.t. Regarding thermal properties, the addition of BNC results in a decrease in T_g and melting temperature, T_m . This is mainly caused by the degradation of PLA.

4.3.3. Starch

Starch is a biopolymer abundant in nature. It contains a high portion of amylose, which consist of linear chains of glucose units, as it is showed in *Figure 28*. It presents poor mechanical properties and high-water affinity. However, it is inexpensive and extensively used in many fields. Different nanocellulose reinforcements can be used in starch composites.

⁴⁶ (Zhao Qian Li, Xiao Dong Zhou, Chong Hua Pei) Preparation and Characterization of Bacterial Cellulose/Poly lactide Nanocomposites.; *Polym.-Plast. Technol. Eng.*, **2010**, 49 (2). DOI: <https://doi.org/10.1080/03602550903284198>

- **Cellulose nano whiskers**⁴⁷ (CNW): composites are created by solution casting and melt blending methods. The starch used here was modified potato starch. Water and sorbitol were used as plasticizers. Nanocellulose whiskers were isolated by acid hydrolysis from microcrystalline cellulose (MCC). The final composites are rough, and their tensile modulus, yield strength and elongation are improved compared to the pure matrix, using 5%wt. of nanocellulose. The elongation at break unexpectedly increases due to the processing of the materials. In addition, the moisture content increases, and it may also increase the elongation at break and the storage modulus.
- **BNC**⁴⁸: these composites were created by film casting. A suspension of pure BNC is made, with amounts varying from 10% to 70% w.t of starch. With the addition of BNC to reinforce the starch matrix, the mechanical properties of the composite are greatly improved. Increasing the amount of reinforcements, the Young modulus and tensile strength of composites increase at the expense of the elongation to break. In addition, the composites show an improvement of the thermo-mechanical properties and the glass temperature increase, so the composites gain thermal stability.

⁴⁷(Ingvild Kvien, Junji Sugiyama, Martin Votrubic, Kristiina Oksman) Characterization of starch-based nanocomposites; *J.I Mat. Sci*; **2007**; 42, p.8163-8171. <https://doi.org/10.1007/s10853-007-1699-2>

⁴⁸ (Nattakan Soykeabkaew, Nittaya Laosat, Atitaya Ngaokla, Natthawut Yodsuwan, TaweeTunkasiri) Reinforcing potential of micro- and nano-sized fibers in the starch-based biocomposites; *Compos.Sci.Technol.*; **2012**; 72 (7), p.845-852. DOI: <https://doi.org/10.1016/j.compscitech.2012.02.015>

4.4. Bio-based polymers ^{49 50 51}

Bio based polymers are polymers which have partial or total renewable building blocks made of renewable feedstock.

Although the production of these polymers is currently small, they will grow to considerable amounts, due to the advance in biomass refining processes. These products can be used for the development of polymer structures with properties such as environmental compatibility, structure variability and flexibility. The development of bio-based materials affirms the principles of Green Chemistry, which are the design and use of products that minimize the generation of pollution and the risk to human health and to the environment.

Main conventional polymers used like polyethylene terephthalate, polyamide and polypropylene can be manufactured from bio monomers-derived glucose fermentation or lignin fermentation, obtaining Bio-PET, Bio-PA and Bio-PP. In *Figure 30*⁵¹, it can be seen that from wastes and non-biodegradable biomass, bio-based plastics can be obtained by fermentation and posterior polymerization. Also, other types of polymers, natural (cellulose) and biopolymers (PLA), can be obtained from wastes and feedstocks.

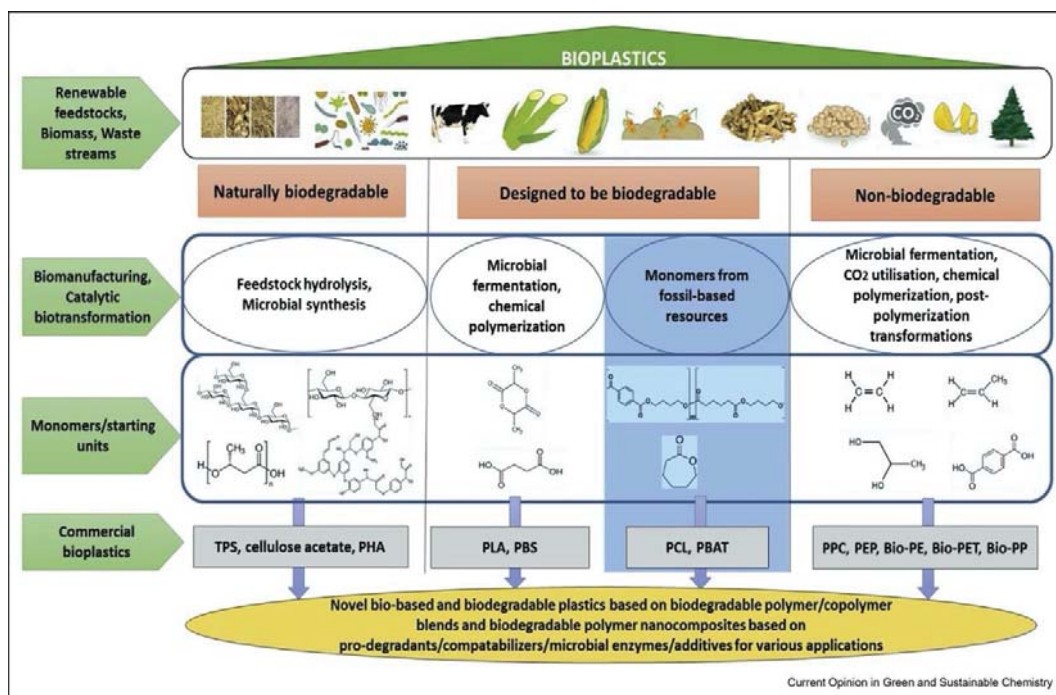


Figure 30: Bioplastics origin and creation from natural resources.

⁴⁹ (Richard D Wool, Xiuzhi Susan Sun) Bio-based Polymers and Composites, First Edition, **2005**; p.1-32. DOI: <https://doi.org/10.1016/B978-0-12-763952-9.X5000-X>

⁵⁰ (Antonio Meraldo) Multilayer Flexible Packing ,Second Edition; *Plastics Design Library* **2016**; p.47-52 DOI: <https://doi.org/10.1016/B978-0-323-37100-1.00004-1>

⁵¹ (Saranya Ramesh Kumar, P. Shaiju, Kevin E. O'Connor, Ramesh Babu P) Bio-based and biodegradable polymers - State-of-the-art, challenges and emerging trends, *Curr.Opin.Green.Sustain.Chem*; **2020**; 21, p.75-81. DOI: <https://doi.org/10.1016/j.cogsc.2019.12.005>

Composites can be designed using only bio-based polymers. They will have specific functionalities suitable for many applications with the addition of completely biodegradable and recyclable fact. Emerging bio-based polymers like poly (ethylene 2,5-furandicarboxylate) (PEF)/poly (trimethylene terephthalate) (PTT) and polypropylene carbonate (PPC) produced from bio-based monomers and alcohols/epoxides respectively, showed considerably good thermal and barrier properties regarding their petroleum counterparts.

The amount of bibliographic studies using bio-based polymers as matrices of nanocomposites is scarce. This is the reason why they are not going to be considered in this project. However, I find interesting to remark the advantages these polymers offer and the possible use of them in new materials.

5. Review

In this section, and overall review of all the composites I mentioned in *sections: 4.2 and 4.3* are going to be discussed. The main purpose is to make conclusions about the aspects along my bibliographic research. *Table 2* presents the most relevant information about the composites. Every system has, type of matrix, type of nanocellulose, process techniques and improvements on the final material.

According to the table, there are a wide number of polymers enrolled in the inclusion of nanocellulose to create new materials. However, I found wider amount of information about PP and PE. Both of them are the matrix of interest in CETIM company and they mainly develop composites with these polymers. Both are present in almost every object of our daily life⁵². As it was commented in *section: 1.1*, they are destined to packing, building and construction, automotive industry etc.

The reason why PP and PE are usually study is their surprisingly characters. They exhibit great stability against chemical substances and high temperatures, they barely absorb water, they can be easily molded, and they are affordable. Supplementary, they can be obtained as bio-based polymers and they last a long time. Due to these facts, many companies use them as object of study for composites.

Regarding nanocellulose, the main types used are cellulose nanofibres and nanocrystals. In almost all the studies, these nanocelluloses are found combined with polymeric matrix. For companies like CETIM, nanocellulose is easy to be obtained and prepared. In addition, nanoparticles provide many advantages, as commented in *section: 3.7*.

It is obvious that nanocellulose modifications are more common than polymers ones. As far as I am concerned, nanocellulose is facile to modify, because of its hydroxy groups. The reagents needed are simple and reactions are feasible in terms of time and procedure. Additionally, the results of nanocellulose modifications are more interesting in composites.

Table 2 shows that the main processed technique of composites is solvent casting. It is commonly used because a good interaction can be achieved between polymers and nanocellulose.

⁵² 'plastic garbage project' URL:<https://www.plasticgarbageproject.org/es/vida-plastico> . (Accessed: 5th June 2020)

Almost all the composites have their properties improved by the inclusion of nanocellulose. It is a fact that mechanical properties are the most improved due to the 'principle of combined action'. Also, thermal properties are significantly improved.

The common percentage of nanocellulose used in polymeric composites is between 2% and 20% w.t. I did not find studies with more than 30% w.t. of nanocellulose in polymers. I suppose that up to 30%, no properties are improved, and the compatibility between phases is not good.

5.1. Overall review table

Table 2: Overall comparison of composites found in the bibliography and different aspects and characteristics.

Ref.	Polymer	Cellulose	Polymer modification	Cellulose modification	Cellulose origin	% of cellulose	Processed technique of composite	Improved composite properties
[16]	PS	CNF		TEMPO oxidation			Solvent casting	Tensile strength Elastic modulus
[38]	PS	CNC		TEMPO oxidation	Cotton		Extrusion	Tensile modulus thermal stability
[37]	PS	CNW				2-16	Solvent casting	
[37]	PP	CN/MC	MA grafting	Silicates	Wood flour		Melting-blending	Mechanical properties
[37]	PP	CNW		Surfactants			Solvent casting	Tensile strength
[37]	PP	NC	Acrylic oligomer		Soybean	0-6	Melting- blending	Tensile strength
[37]	PP	NC	MA grafting			0-15	Solvent casting	Tensile strength
[39]	PE	CNW		Acid hydrolysis	Ramie	0-15	Extrusion	Tensile strength
[8]	PET	CNC		Surfactants		0-15	Wet laid nonwoven	Thermal stability



[8]	PET	CNF		Compatibilizer PEG		0-15	Coating	Tensile strength Thermal stability
[40]	PA	CNW		Acid hydrolysis	Cotton	1	Coating	Thermal stability
[42]	PHB	CNC	Modifiers TB and A		Sigma Aldrich®	2-4	Solvent casting	Thermal stability
[42]	PHB	BNC				2-4	Solvent casting	Thermal stability
[43]	PHBv	BCNW		Compatibilizer PEG		2-3	Solvent casting	Mechanical properties
[44]	PHBv	CNC				3-20	Solvent casting	Thermal stability
[45]	PLA	CNF			Lignocellulosic materials	3	Injection molding	Decrease in moisture absorption
[45]	PLA	CNC	MA grafting	Syllation	Minerals	5-35	Extrusion	Mechanical properties
[46]	PLA	BNC		MA grafting		10	Solvent casting	Tensile strength
[47]	Starch	CNW	Plasticizers		Potato	5	Solvent casting	Mechanical properties
[48]	starch	BNC				10-70	Film casting	Mechanical properties Thermal stability

6. Proposal of progress

In light of the current situation with Covid-19, the use of polymers has become more and more important. They are particularly suitable for medical applications, from exam gloves to sterile syringes and adhesive bandage. Thanks to their barrier properties, they are perfect materials against contamination. However, mainly of these items are disposable. My personal view regarding the overall project I have been working on is to achieve circulation of thermoplastic materials. Reaching biodegradable thermoplastics with improved properties by inclusion of nanocellulose, we would be able to reuse, recycle and recovery them.

Another interesting point is the possible addition of other wood derivatives such as lignin. In fact, I personally performed derivatization reactions with lignin also in CETIM during my external practical lessons. I did sulfomethylation and esterification of lignin to modify its hydrophobic nature and to improve the compatibility with polymeric matrices. This results in an improvement in thermal, mechanical and barrier properties of thermoplastics just like with nanocellulose. During these practical lessons, the composites created had an extra dispersed phase, glass fibres. This could also be useful in thermoplastics composites with nanocellulose. The addition of an extra phase could add new properties to the composite. Furthermore, the reinforcement phase could have a natural origin like nanocellulose.

Timeframe

2-mar	Bibliographic research in CETIM company
3-mar	Bibliographic research in CETIM company
4-mar	Bibliographic research in CETIM company
5-mar	Bibliographic research in CETIM company
6-mar	Bibliographic research in CETIM company
7-mar	Bibliographic research in CETIM company
8-mar	Bibliographic research in CETIM company
9-mar	Introduction to CETIM laboratories
10-mar	Sililation reaction using mecanical CNF
11-mar	Obtention of nanocellulose from cellulose pulp
12-mar	Sililation reaction using mecanical CNF
13-mar	Lockdown: change of TFG into a bibliographic research
14-mar	
15-mar	
16-mar	Nanoellulose types
17-mar	Nanocellulose types
18-mar	Nanocellulose modifications
19-mar	Nanocellulose modifications
20-mar	Nanocellulose modifications
21-mar	
22-mar	
23-mar	Nanocellulose modifications
24-mar	Nanocellulose modifications
25-mar	Composites improvements due to addition of nanocellulose
26-mar	Polymer types
27-mar	Polymer types
28-mar	
29-mar	
30-mar	Polymer types
31-mar	Polymer types
1-abr	Processing techniques of composites
2-abr	Processing techniques of composites
3-abr	First modification by my advisors
4-abr	Easter
13-abr	Easter
14-abr	CETIM information
15-abr	Foreword
16-abr	Foreword
17-abr	Foreword
18-abr	
19-abr	
20-abr	Polymer modifications
21-abr	Polymer modifications



22-abr	Polymer modifications
23-abr	Convectional polymers and their composites with micro/nanocellulose
24-abr	Convectional polymers and their composites with micro/nanocellulose
25-abr	
26-abr	
27-abr	Biopolymers composites with different cellulose fibres
28-abr	Biopolymers composites with different cellulose fibres
29-abr	Biopolymers composites with different cellulose fibres
30-abr	Biopolymers composites with different cellulose fibres
1-may	Labor day
2-may	Second modification by my advisors
3-may	
4-may	Composites, fibres and matrices types
5-may	Composites, fibres and matrices types
6-may	Composites, fibres and matrices types
7-may	Composites, fibres and matrices types
8-may	Composites, fibres and matrices types
9-may	
10-may	
11-may	Bio-based polymers
12-may	Bio-based polymers
13-may	Bio-based polymers
14-may	Bio-based polymers
15-may	Bio-based polymers
16-may	
17-may	
18-may	Review and review table
19-may	Review and review table
20-may	Review and review table
21-may	Review and review table
22-may	Review and review table
23-may	Review and review table
24-may	Review and review table
25-may	Review and review table
26-may	Review and review table
27-may	Review and review table
28-may	Review and review table
29-may	Review and review table
30-may	
31-may	
13-jul	Third correction by my advisors
14-jul	Final modifications
15-jul	Final modifications



16-jul	Final modifications
17-jul	Final modifications
18-jul	Final modifications
19-jul	Final modifications
20-jul	Final modifications