UNIVERSITAT POLITÈCNICA DE CATALUNYA
BARCELONA**TECH**
Escola Superior d'Agricultura de Barcelona

Preparation and Characterization of PMMA/CNFs nanocomposite

Grau en Enginyeria de Biosistemes – Final Project

MARC RAMÓN MORENO

Directors:
Mónica Ardanuy
Josep Claramunt

24/07/2019

Contents

Acknowledgement

I would like to acknowledge my parents and my friends for all the aid provided that actually help me a lot to finish this work. Besides that, I would also like to acknowledge the members of my research group and both of tutors for the contributions and advices given during the process

Resum (CAT)

Les Nanofibres de cel·lulosa (NFC) són nanomaterials cel·lulòsics transparents i vermiformes que exhibeixen una superfície remarcable, així com una amplària nanomètrica que proporciona innombrables propietats reològiques i mecàniques. D'altra banda, la naturalesa fràgil i rígida del polimetilmetacrilat (PMMA) dificulta la promoció d'aquest material per a aplicacions noves i innovadores. Per tant, en aquest treball final de grau es pretén incorporar diferents percentatges en pes de NFC oxidades amb TEMPO (Tetramethyl-piperidinyloxyl) en una matriu de PMMA amb la finalitat d'obtenir diversos tipus de nanocomposits de NFC/PMMA. La carboxilació TEMPO redueix el nombre de grups alcohol que jeuen en la superfície d'aquestes fibres millorant, en conseqüència, la dispersió d'aquestes mateixes al llarg de la matriu que porta com a resultat una millora en quant a la transparència. El test mecànic mostra que amb un contingut de NFC elevat el material exhibeix una ductilitat alta però una resistència baixa. Malgrat això, a un contingut reduït de NFC la ductilitat no va perdre intensitat i la tenacitat del material gairebé va romandre intacta en comparació amb la del PMMA pur. Finalment, l'anàlisi òptica mostra clarament que amb un contingut elevat de NFC la transmitància es redueix dràsticament, encara que amb un contingut menor la transparència pot ser gairebé igual respecte al PMMA pur.

Paraules clau: Nanofibres de cel·lulosa, polimetilmetacrilat, nanocomposit, carboxilació TEMPO, ductilitat, tenacitat

Resumen (ESP)

Las nanofibras de celulosa (NFC) son nanomateriales celulósicos transparentes y vermiformes que exhiben una superficie remarcable, así como una anchura nanométrica que proporciona innumerables propiedades reológicas y mecánicas. Por otro lado, la naturaleza frágil y rígida del polimetilmetacrilato (PMMA) dificulta la promoción de este material para nuevas e innovadores aplicaciones. Por lo tanto, en este trabajo final de grado se pretende incorporar diferentes porcentajes en peso de NFC oxidadas con TEMPO (Tetramethyl-piperidinyloxyl) en una matriz de PMMA con el fin de obtener varios tipos de nanocomposites de NFC/PMMA. La carboxilación TEMPO reduce el número de grupos alcohol que yacen en la superficie de estas fibras mejorando en consecuencia la dispersión de estas mismas a lo largo de la matriz que llevara como resultado una mejora en cuanto a la transparencia. El test mecánico muestra que con un contenido de NFC elevado el material muestra una ductilidad alta pero una resistencia baja. A pesar de esto, a un contenido reducido de NFC la ductilidad no perdió intensidad y la tenacidad del material casi quedo intacta en comparación con el PMMA puro. Finalmente, el análisis óptico muestra claramente que con un contenido elevado de NFC la transmitancia se reduce drásticamente, aunque con un contenido menor la transparencia puede ser casi igual con respecto al PMMA puro.

Palabras clave: Nanofibras de celulosa, polimetilmetacrilato, nanocomposite, carboxilación TEMPO, ductilidad y tenacidad.

Abstract (ENG)

Cellulose nanofibres (CNF) are hollow transparent and rod-like tailored cellulosic nanomaterials that exhibit a remarkable surface area as well as a nanometric width which render numerous rheological and mechanical properties. Conversely, poly(methyl methacrylate) (PMMA) with a rather brittle nature and rigidity hamper the fostering of these material for new cutting-edge applications. Therefore, in this bachelor's final work is pretended to embed different TEMPO-oxidized CNFs weight percentages into a PMMA matrix in order to obtain various type of CNF/PMMA nanocomposites. TEMPO-carboxylation aims to reduce the number of alcohol groups lying in the surface of these fibres enhancing, consequently, their dispersion all along the matrix which results in an improvement of the material transparency. The mechanical tests show that at a higher CNFs content the material display a great ductility but a paltry toughness. Contrarily, with a reduced CNFs content the ductility was not diminished, and the material toughness was almost kept unchanged in comparison with the pristine PMMA. Finally, the optical analysis clearly shows that for higher CNFs content the transmittance was drastically reduced, yet at a lower CNFs content transparency was almost unamended as regard the neat PMMA.

Keywords: Cellulose nanofibres, poly (methyl methacrylate), nanocomposite, TEMPO-carboxylation, ductility, toughness

1. Introduction

1.1. Project's justification and scope

The main idea of final project is to fuse Poly (methyl methacrylate) (PMMA) and nanocellulose fibres to acquire a mechanically improved composite.

The suitability of this thesis comes from PMMA stiffness and rather brittle nature. Project's scope is the extraction of cellulose nanofibers from the vegetal material, surface modification of CNFs to achieve a better mixing with the PMMA matrix, composite manufacture and optomechanical characterization.

In this thesis, processing of CNFs and assembly of the composite is carried out together with its optomechanical evaluation.

There are existing many interim steps that are not included in this thesis but are, indeed, truly important and critical for the success of the composite enhancement. Many key steps have been reported to be considerable recommended to achieve high quality CNFs, some of these are purification, mechanical pre-treatment, biological/chemical pre-treatment and principal mechanical treatment. Within each step, many ways might be found to be able to satisfy which is requested.

Once CNFs have been pulled out from the pulp, a TEMPO-mediated oxidation, which is a sort of carboxylation, was the chemical process chosen to modify the surface of the CNFs. This is one way to ease CNFs delamination and defibrillation, yet some others are awaiting to be discovered, but currently, these one is the simplest and most economically suitable. Despite these facts, there are other few existing paths which may be even more interesting than the method recently mentioned.

Functionalising via chemical modification through covalent bonding or functional groups could be also a more competent yet skilful procedure, enabling a more powerful interaction between both items that are adjoining in the composite.

Combining all these methods to be undergone by the CNFs might be key factor to obtain a fully functionalised CNFs prepared to be assembled perfectly in any sort of hydrophobic matrix.

1.2. Objectives

The objective of this bachelor’s final project is to achieve a mechanically improved nanocomposite maintaining the optical properties of PMMA. With this in mind, the following targets have been considered:

- To merge PMMA with CNF without reverse coalescence so that a scattered PMMA/CNF nanocomposite displaying a random percolated CNFs framework could be assembled.
- To reduce the brittleness of the PMMA/CNF nanocomposite by improving upon the ductility of the material without other mechanical parameters being amended as a result of this.
- To obtain the aforementioned PMMA/CNF nanocomposite without the characteristic clearness and transparency of PMMA being affected by the presence of CNFs.

2. State of the art and referents

2.1. Approach to PMMA

2.1.1. Description of PMMA

Poly (methyl methacrylate) is the most commonly known example of an acrylic plastic. Acrylic plastics are those whose base polymers are polymers of acrylic acid or polymers of monomers structurally originated from acrylic acid or are acrylic acid copolymers or its derivates with other monomers. (Harper and Petrie, 2003)

Methacrylate esters is the collective noun given to those acrylic acid-derived monomers. Alongside with methyl methacrylate, ethyl methacrylate, n-butyl methacrylate as well as iso-butyl methacrylate and 2-ethylhexyl methacrylate may also be used as acrylic polymers. (Gooch, 2011)

PMMA (Poly methyl methacrylate), shown in figure 1, is the mostly used thermoplastic polymer. Thermoplastics are non-crosslinked polymeric materials able of being successively softened or melted by increasing temperature or solidified by decreasing temperature. (Harper and Petrie, 2003)

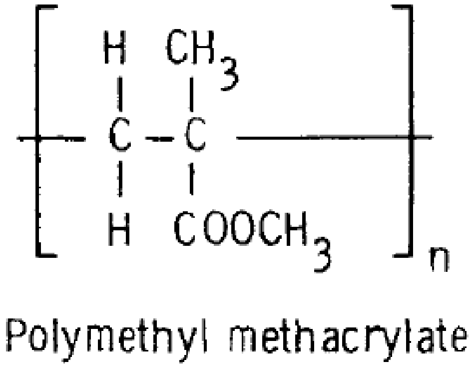

Figure 1. Chemical structure of Polymethyl methacrylate.(Harper and Petrie, 2003)

2.1.2. Properties of PMMA

PMMA is an amorphous polymer since no crystallization phenomena is observed during solidification process, whereupon no spherulite presence will appear in its inner structure. In virtue of this, PMMA is a colourless polymer whose density is 1.19 g/cm^3 and whose glass transition temperature is 120ºC.(Harper and Petrie, 2003; D.Bashford, Chapman and Hall, 1997; Ali, Karim and Buang, 2015; Pawar, 2016)

PMMA is regarded as noticeable materials for their remarkable optical properties such as refractive index or transmittance. PMMA 3mm thick layer is able to transmit up to 92% of visible light and the refractive index ranges similar values than that of glass.(Pawar, 2016) Besides, PMMA is resistant to sunlight as UV radiation does not alter its molecular structure.(Harper and Petrie, 2003; Ali, Karim and Buang, 2015)

Despite this, PMMA brittleness may suppose the foremost challenge. The mainly cause of this phenomenon are the pendent groups portrayed in the figure 1.(Harper and Petrie, 2003; Brydson, 1989; Campo, 2006; Osswald, T., Baur, E., Brinkman, S., Oberbach, K., Schmachtenberg, 2006)

These same bulky structures are also to be blamed for avoiding crystallization which is the reason behind PMMA amorphous nature. Perhaps, pendent groups are the cause of stiffness and fragility since they block neighbouring functional groups of the backbone chain eluding any kind of interchain shifting.(Harper and Petrie, 2003; Brydson, 1989; Campo, 2006; Osswald, T., Baur, E., Brinkman, S., Oberbach, K., Schmachtenberg, 2006)

Table 1. Summary of properties of PMMA.

Property	PMMA	References
Water Absorption (%)	0.3	(D.Bashford *et al.*, 1997)
Thermal conductivity at 20ºC (W/mK)	0.12	(U.Ali *et al.*, 2015)
Tensile strength (MPa)	72	(U.Ali *et al.*, 2015)
Tensile modulus (GPa)	3.10	(U.Ali *et al.*, 2015)
Flexural strength (MPa)	103	(D.Bashford *et al.*, 1997)
Flexural modulus (GPa)	3.3	(D.Bashford *et al.*, 1997)
Elongation at Break (%)	5	(D.Bashford *et al.*, 1997)

As depicted in table 1, PMMA shows a paltry elongation at break which reveals this abovementioned brittleness, although these remarkable flexural and the tensile modulus means to say that PMMA is a tough material and seemingly one of the hardest plastics with considerable notch-resistant features.

In addition, outstanding thermal insulation can be achieved by virtue of PMMA low thermal conductivity.(Harper and Petrie, 2003; Ali, Karim and Buang, 2015)

2.1.3. PMMA Production

PMMA can be prepared and handled in numerous forms such as rods, sheets as well as tubes ready to be machined and bonded or in a bead form which is usually used as conventional processing via extrusion or injection moulding. (Harper and Petrie, 2003)

This manufactures ready-to-use forms are created via in situ polymerization by casting pre-polymerized monomers and adding organic hydroperoxides or peresters to trigger free radical polymerization.(Harper and Petrie, 2003)

This technique is on the need of those in charge of producing considerable rubber plateau materials and bulky polymerized materials with generally high molecular weight. Hence, this method is put into practice for making bathtub materials such as whirlpool baths, showers and domestic decorative items.(Harper and Petrie, 2003)

On the other hand, acrylic plastic bead form is made via suspension polymerization which produces such a low molecular weight material that enables melt processing via injection moulding, casting extrusion, or vacuum and pressure forming.(Harper and Petrie, 2003)

2.1.4. Applications of PMMA

At the sight of these excellent properties, the fact that acrylic density is half less than that of glass (Pawar, 2016) and the exceptional resistance to inclement weather and chemical abrasion, except for some organic solvents, PMMA has mainly served as a noteworthy shatterproof substitute of glass in many applications like automotive rear lights assemblies, lenses, aircraft cockpits, as well as dentures, windshields, steering wheel bosses and many architectural materials. (Harper and Petrie, 2003)

Moreover, despite not having such a tough nature as that of polycarbonate, PMMA does not contain Bisphenol-A, which is known beforehand to be dangerously harmful for the human health. Instead of this, PMMA have higher environmental stability than polystyrene and polyethylene. (Pawar, 2016)

In architecture and construction, PMMA is used in door and window profiles for its great chemical, UV and impact resistance. In many greenhouses and plant growth facilities PMMA is present in the overall structure due to its outstanding light transmission. Acrylic glass is also used in fish facilities and aquaria as multi-skin and corrugated sheets which are incredibly tough. (Pawar, 2016)

Acrylic resins play a major role in automotive industry, one instance might be the presence of PMMA in automotive glazing as a lightweight material with insulating properties and exceptional malleability which enable new suitable designs to be rolled out at ease. (Pawar, 2016)

PMMA can also be in many other kinds of moulded pieces such as interior and exterior panels, fenders, trims or bumpers. In other related industries within the transportation sector, acrylic glass is also a very useful material. One such example may be the use of this polymer for manufacturing windscreens, windows and aircraft canopies for any sort of planes and aerial devices since PMMA is able to resist high inside cabin pressure, cold temperatures and UV radiation. (Pawar, 2016)

In electronics, PMMA is chosen for remarkable durability and optical properties. Those afore-revealed features could be the reason behind acrylic’s presence in countless electronical devices such as control panel fascia, appliance parts, LCD screens and monitors, as well as mobile phone screens, TV and equipment fascia and so forth. (Ali, Karim and Buang, 2015; Pawar, 2016)

Acrylic polymers are, certainly, in mind of those concerned about materials selection for photovoltaic module’s manufacture as a result of PMMA’s rather transparent and resilient nature.(Ali, Karim and Buang, 2015) (Pawar, 2016)

As mentioned before, in home furnishing and decorative furniture such as chairs, tables, diverse homeware, as well as tablemats, cutlery among many other tableware items, PMMA withstands on enduring basis for being one of the most utilized materials in this domain. (Pawar, 2016)

Material lightning designers are used to take profit from acrylic’s aesthetical resemblance to glass and optomechanical attributes that enables to machine ceiling lightweight lights, pendant luminaires support, table lamp supports, as well as floor lamps fascia and wall lights fascia among others. (Pawar, 2016)

Apart from this, one ought to highlight acrylic’s compatibility with the human tissue which brings the chance to bear with many issues within the biomedical healthcare industry. As proof, in orthodontics many cavities are filled with this polymer that ensures outstanding bonding capabilities, excellent dimensional stability and remarkable malleability. (Ali, Karim and Buang, 2015; Pawar, 2016)

Another example might be acrylic’s usage in optometry wherein the patient is operated on for cataracts by removing patient’s intraocular lenses and replace them with an artificial lenses usually made of PMMA. (Pawar, 2016; Ali, Karim and Buang, 2015)

In addition to that, PMMA has been harnessed as bone cement because of the modulus of elasticity is similar to that of bones. (Ali, Karim and Buang, 2015)

PMMA might be under several names given by the major suppliers such as Plexiglas by ElfAtochem, Cyrolite by CYRO, as well as Optix by Plaskolite, Perspex by ICIAcrylics and NAS and Zylar by Nova Chemicals. (Harper and Petrie, 2003)

2.1.5. Summary of PMMA

Acrylic polymers offer a wide range of advantages and disadvantages. Certainly, acrylics state many weak points, amongst them, one should mention the fact that PMMA may be strongly damaged by powerful solvents, or that load bearing parts may not be able to be proof against such a huge load as it is expected. (Harper and Petrie, 2003)

On top of that, acrylic’s thermal expansion coefficient is higher than that of glass leading to a paltry thermal stability or the fact that bulky highly polymerized moulded structures can be highly stressed as these pieces have to undergo a solvent welding process which could cause some sort of degradation. (Harper and Petrie, 2003)

In spite of this, PMMA has great optical clarity, excellent weatherproof properties, underrated stiffness, as well as hydrophobic nature, optimal electrical traits, slow burning rate and low moisture expansion coefficient. (Harper and Petrie, 2003)

2.2. Approach to CNFs

2.2.1. Description of CNFs

Cellulose nanofibers (CNF), sometimes misunderstood as nanofibrillated cellulose (NFC) might be defined as a scattered yet substantially entangled cluster of fibrils characterised by presenting a nano-scale width which renders an upcoming variety of properties like high Young's modulus, high tensile strength, great entanglement and outstanding film-forming capacity as well as long aspect ratio and so large surface area.(Abitbol *et al.*, 2016; Mishra, Sabu and Tiwari, 2018)

The latter aforementioned properties, long aspect ratio and large surface area, alongside with a hydrophilic nature mark these fibres by giving them outstanding water-grasping traits which provides a thixotropic nature to those aqueous solutions in which these fibres are present.(Innventia AB, 2017) This comes down to the fact that the viscosity of CNF mild aqueous solution varies as regards the duration and scale of the applied shear forces.(Nechyporchuk *et al.*, 2018)

Furthermore, the rheological properties that these fibres are able to exhibit are unique, namely the outstanding viscosity and the remarkable storage modulus far beyond the critical solubility concentration.(Innventia AB, 2017)

These hereinbefore mentioned traits have been studied all along these recently past few years, yet anybody came up with any conclusion. Particularly, it has been found out that the temperature was not capable of altering significantly the rheological features of these fibres. Despite this, few behavioural changes such as less viscosity and entanglement have been observed when the temperature was increased. This might be possible due to a reduction in water viscosity or lesser fibre swelling effect of CNFs as they present a powerful bias for moisture absorption. (Innventia AB, 2017)

Nanocellulose fibres are a bundle of rod-like cellulosic material which may differ in their fundamental properties in accordance with the raw material source and the extraction procedure employed.(Thomas *et al.*, 2018)

Thus, nanofibrillated cellulose breeds the concept of nanocellulose. It has been reported in the literature that nanocellulose concept refers to those cellulosic extracts or tailored materials that possess at least one nanometric dimension.(Mishra, Sabu and Tiwari, 2018)

This would mean to say that some other sorts of cellulosic materials can be isolated from nature. Cellulose nanocrystals (CNC), also called cellulose nanowhiskers (CNW), are another type of crafted cellulosic material which has been plentifully used as reinforcing material and so forth. (Abitbol *et al.*, 2016)

Cellulose displays two varieties of chain-referred domains: the crystalline region and the amorphous one. As it is displayed in the figure 2, the crystalline region is depicted as an organized structure meanwhile the amorphous region is portrayed as a random structure. (Mishra, Sabu and Tiwari, 2018)

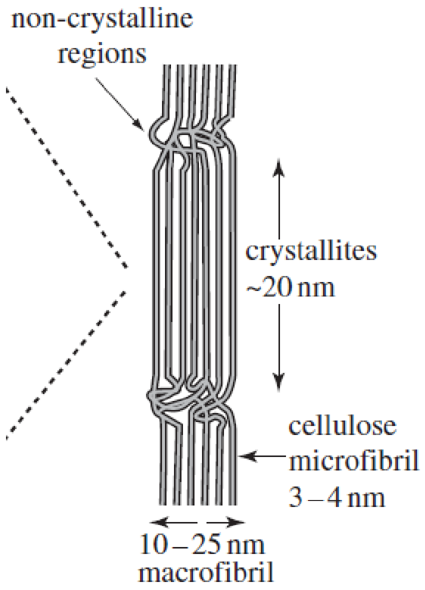

Figure 2. Cellulose crystalline and amorphous regions.(Gibson LJ, 2012)

Unlike CNCs, CNFs exhibit both sorts of phases combining the properties of either structures (Mishra, Sabu and Tiwari, 2018), this fact provides a more powered entanglement, and so gives better reinforcing effect.(Xu *et al.*, 2013)

Bacterial cellulose is another kind of cellulosic substance that is biosynthesized by *Gluconacetobacter xylinus.* This situation gives rise to a rather more human controlled environment where this material can be previously designed and engineered just by altering the biochemical pathways belonging to cellulose production. In spite of this, this product is not as available and affordable as other kinds of hereinto described cellulosic matters.(García *et al.*, 2016)

On account of the fact that there are existing different sources of cellulose, there are also existing different types of crystalline cellulose. Heretofore, two distinct polymorphisms had been found according to hydrogen bonding design: cellulose Iα, which is obtained from bacteria together with algae, as well as cellulose Iβ, which can be isolated from plants. (Mishra, Sabu and Tiwari, 2018)

Hydrogen-bond network conformation discriminate between one kind of cellulose and the other, which differ among themselves as regards their source and their biosynthesis pathways. Those abovementioned differences lie in the type of crystalline polymorphism, the width and length of the fibre, the proportion of amorphous regions and crystalline ones. (Mishra, Sabu and Tiwari, 2018)

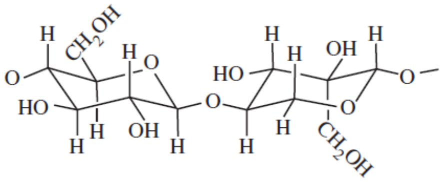

Figure 3. Molecular structure of cellobiose.(Gibson LJ, 2012)

Cellulose is one of the most ubiquitous and renewable polymers in the biosphere. Cellulose biogenesis is the biological pathway that produces all kinds of cellulose, which means that this biochemical route is present in plants, algae, certain animals like tunicates as well as bacteria. (Thomas *et al.*, 2018)

Cellobiose, which is the unique repeated monomer present in the backbone chain of cellulose, is made up of β-D-glucopyranose units that are joined together by β-1,4 linkages as shown in the figure 3.(Gibson LJ, 2012)

Individual cellulose polymer chains gather together in order to make up primary fibrils through intermolecular hydrogen bonds and hydrophobic interactions. This stems from the high degree of hydroxylation along the polymer chain which provokes the appearance of hydrogen bonds within the intrinsic cellulose molecule and between vicinal cellulose chains.(Gibson LJ, 2012)

This latter intermolecular hydrogen bonds are blamed for being the reason behind fibrillar and semi-crystalline packaging structures which provides these outstanding herein described traits of cellulose. (Thomas *et al.*, 2018)

Once these primary fibrils are contained, they assemble themselves in order to generate microfibrils which additionally combine to became a larger macroscopic cellulose fibre as displayed in the figure 4 *(c)*. (Mishra, Sabu and Tiwari, 2018; Thomas *et al.*, 2018)

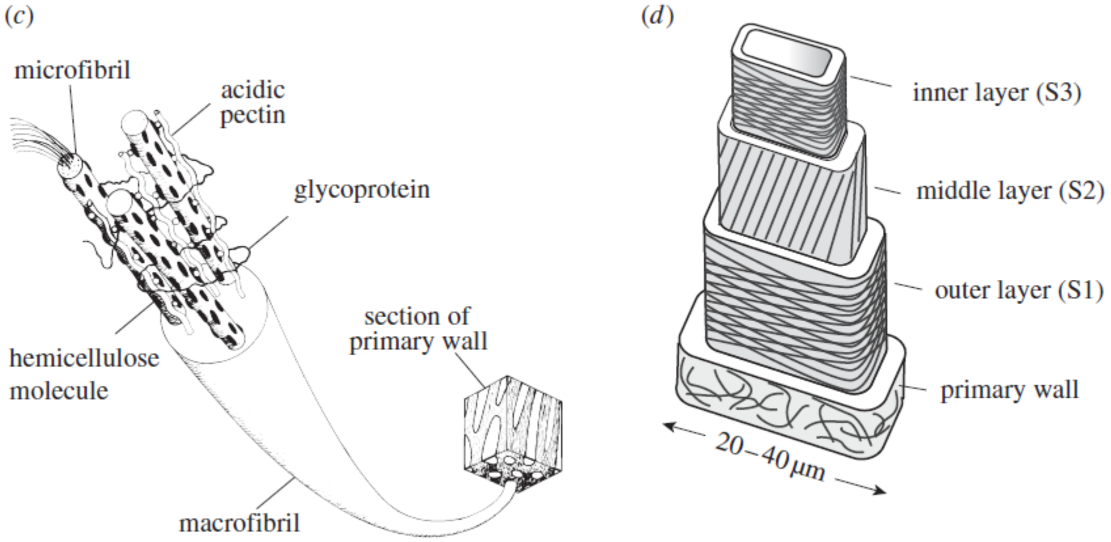

Figure 4. (c) Macrofibril coming out of a primary cell wall; (d) layered cell wall of wood.(Gibson LJ, 2012)

In the figure 4 *(d)* it can be observed a layered cell wall which could be part of wood or part of a higher plant. This cell wall is comprised of lining as a matrix body which is reinforced by this hereto recently mentioned cellulose macrofibrils acting itself as a composite. As it is portrayed in figure 5, hemicellulose behave like a binding agent aiding and improving the association between lignin and cellulose.(Mishra, Sabu and Tiwari, 2018; Thomas *et al.*, 2018) This commonly known as the hierarchical structure of cellulose.

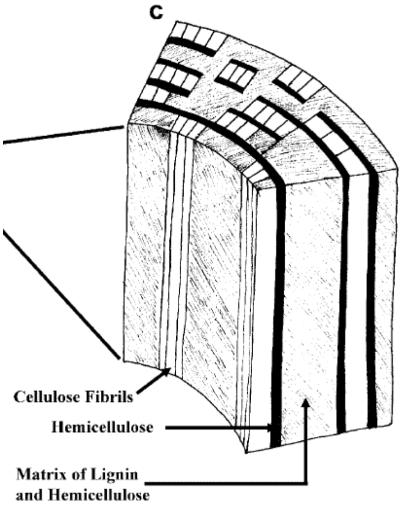

Figure 5. Layered middle layer of cell wood.(Pérez et al., 2002)

2.2.2. CNFs isolation

Isolation and functionalization are a watershed in the overall process of cellulose nanofibrils production and conditioning.

Cellulose is the most omnipresent natural polymer on the biosphere, therefore cellulose reservoirs can be classified as regards the human feed-stock selection.(García *et al.*, 2016)

Primary cellulose reservoirs are those wherein cellulose fibres are the main product and purpose. In fact, just considering vegetal natural fibres, another division regarding different cellulose sources might be done. (García *et al.*, 2016)

Several types of vegetal fibres that are used for the extraction of CNFs can be divided in different categories: *Bast fibres* such as jute, flax, hemp, ramie and kenaf; *seed fibres* like coir, cotton and kapok; *grass fibres* and *reed fibres* namely wheat, corn as well as rice; *leaf fibres* as for instance abaca, sisal and pineapple and *core fibres*, for example kenaf, hemp as well as jute. Wood and roots could be included within this classification.(García *et al.*, 2016)

Secondary cellulose reservoirs are basically processed wastes which came from the use, conversion and transformation of cellulosic biomass such as pulp, bagasse, food residues like peelings as well as husks and so on.(García *et al.*, 2016)

Once the source of cellulose is chosen, some compulsory pre-treatments must be carried out just to get rid of non-cellulosic materials namely hemicellulose, pectin and lignin since they could meddle in the process altering the quality, morphology and so the properties of nanocellulose fibres. (Nechyporchuk *et al.*, 2018)

This mandatory purification treatments consist of delignification or pulping, which is a cumbersome process that intends for weeding any kind of non-cellulosic matter out of the biomass itself by forcing this latter to undergo some thermochemical reactions. Bleaching is also a purification process that targets lignin eradication.(Nechyporchuk *et al.*, 2018)

A part from these two recently mentioned methods, another techniques such as sulphite process, Kraft process, sodium hydroxide, hydrochloric acid, hydrogen peroxide, as well as acetic acid treatment, sodium chlorite and potassium treatments are other procedures already used whereby this non-cellulosic substances are also destroyed. (Nechyporchuk *et al.*, 2018)

The manners and means through which nanocellulose is isolated from plant material bring about changes in CNFs morphology and the properties thereof. Hence, a key part therein is the election of the principal mechanical treatments which will render many valuable traits to CNFs. (García *et al.*, 2016)

CNFs are produced by delaminating cellulosic fibres via high mechanical shearing activity, thereby interfibrillar hydrogen bonds of both amorphous and crystalline regions will collapse yielding this very same fibrils.(Kalia *et al.*, 2014)

This mechanical disintegration is seldom performed under tinder-dry conditions since it may give rise to fibre shredding, whereupon CNFs will be yielded with paltry mechanical properties. Thus, CNFs are usually isolated in aqueous mild medium wherein interfibrillar hydrogen loosens intensity avoiding at the same time any sort of reverse coalescence. (Nechyporchuk *et al.*, 2018)

High pressure homogenization and grinding are both the most commonly used top-down mechanical methods. Whilst high pressure homogenization is performed with homogenizers and microfluidizers, grinding is obviously carried through with grinders.(Nechyporchuk *et al.*, 2018)

In order to bring forth high pressure homogenization by using a homogenizer, cellulose diluted slurry should be forcefully pushed into a tight gap which consist of the homogenizer valve and the impact ring. The homogenizing valve and the impact ring operate in a concomitant way by submitting and subjecting the fibers to high shear and impact forces which will lead to ensuing fibrillar delamination.(Kalia *et al.*, 2014)

Fibrillation occurs according to the applied pressure and the number of homogenization cycles. The more pressure is applied, the better will be the disruption efficiency per pass through the homogenizer and the lesser homogenization cycles will be needed. (Kalia *et al.*, 2014)

Microfluidization is also another sort of homogenizing strategy wherein cellulosic slurry is forced through a Z or Y shaped and narrow channel. Thus, high shear and cavitation forces ,which appear conjointly as a result of intense particle collision and high pressure applied, ensue the intended nanofibrillation.(Kalia *et al.*, 2014; Nechyporchuk *et al.*, 2018; Rol *et al.*, 2019)

High pressure homogenization above-said techniques partake of the same purpose which is the fact of producing as much impact and shear forces as possible just to yield CNFs in large quantities. In order to generate this kind of forces, high differential pressure need to be guaranteed since it might induce the formation of gas bubbles that later will implode inwardly provoking the arising of cavitation phenomena and shockwaves that may lead to some kind of cellulose wall disruption.(Kalia *et al.*, 2014)

Whilst high pressure homogenization endures a noticeable likelihood of clogging, grinders are utterly exempt from this. Thereby, ultrafine friction grinding is considered a pioneering technique that means to bring strong shear forces to diluted cellulosic slurries by compelling this very same suspensions between two grooved rough-hewn and coarse-grained grinding disks, one static and the other rotary. (Kalia *et al.*, 2014; Nechyporchuk *et al.*, 2018; Rol *et al.*, 2019)

Certainly, these stones may be brought even more closer without clogging troubles as the fibre size decreases per pass through the grinder and the hard surfaces need to be always in contact to make sure the requested defibrillation. (Kalia *et al.*, 2014; Nechyporchuk *et al.*, 2018; Rol *et al.*, 2019)

A part from this, many other procedures also have been already put in practice, as proof some instances could be extrusion, blending, ultrasonication, cryocrushing, as well as steam explosion, ball milling, aqueous counter collision and so on and so forth.(Nechyporchuk *et al.*, 2018)

Nevertheless, literature's findings concur with the fact that yielding CNFs by only making use of mechanical methods might suppose a huge energetic demand. Therefore, several chemical and biological pre-treatments have been designed to lessen this energetic requirements.(Nechyporchuk *et al.*, 2018)

As for instance, TEMPO-mediated carboxylation clearly proves to reduce energetic consumption. Tetramethyl-piperidinyloxyl (TEMPO) is a steady nitroxyl radical commonly used for acting as a catalyst for the conversion of primary alcohols to aldehydes and carboxylic acids afterwards.(Saito and Isogai, 2004; Isogai, Saito and Fukuzumi, 2011; Rodionova, Eriksen and Gregersen, 2012; Kalia *et al.*, 2014)

In mild aqueous solutions, TEMPO develops at once with NaBr, which is another catalyst, a regioselective oxidation of carbohydrate primary alcohols to carboxyl functional groups with the aid of a primary oxidizing agent as NaOCl. (Saito and Isogai, 2004; Isogai, Saito and Fukuzumi, 2011; Rodionova, Eriksen and Gregersen, 2012; Kalia *et al.*, 2014)

Heretofore, some assumptions were considered just to display an explanation that could enlighten us about this great improvement in defibrillation process in the wake of TEMPO carboxylation application.

The first hypothesis and the most accepted one deals with the fact that TEMPO oxidation create negative charges that give rise to repulsive forces among microfibrils which concomitantly enhance the loss in microfibrils cohesion that was keep by hydrogen bonds. (Saito and Isogai, 2004; Isogai, Saito and Fukuzumi, 2011; Rodionova, Eriksen and Gregersen, 2012; Kalia *et al.*, 2014; Isogai and Bergström, 2018)

Another theory reasoned that TEMPO oxidation improves hydration and so swelling of fibres per se, so that fibres became more elastic and rather more available than previously.(Saito and Isogai, 2004; Isogai, Saito and Fukuzumi, 2011; Rodionova, Eriksen and Gregersen, 2012; Kalia *et al.*, 2014; Isogai and Bergström, 2018)

In spite of the abovementioned, it has also been verified that the degree of polymerization clearly decreased when the oxidation levels were risen, even though cited works highlight the utmost importance of the oxidation level role in lowering the energy input as well as enhancing transparency degree and the ease of delamination.(Saito and Isogai, 2004; Isogai, Saito and Fukuzumi, 2011; Rodionova, Eriksen and Gregersen, 2012; Kalia *et al.*, 2014; Isogai and Bergström, 2018)

On the basis of that view, it is concluded that the greater the carboxyl content is the higher will be the degree of fibrillation and the clearer will also be the CNFs suspension.(Saito and Isogai, 2004; Isogai, Saito and Fukuzumi, 2011; Rodionova, Eriksen and Gregersen, 2012; Kalia *et al.*, 2014; Isogai and Bergström, 2018)

Another example which has also been broadly reported elsewhere (Kalia *et al.*, 2014; Nechyporchuk *et al.*, 2018; Thomas *et al.*, 2018; Rol *et al.*, 2019) is enzymatic hydrolysis. It is known beforehand that this pre-treatment is an environmentally friendly option that could be perfectly applied in lieu of TEMPO-mediated oxidation.(Kalia *et al.*, 2014)

Mild enzymatic hydrolysis is carried out by cellulases. This enzymes can be classified according to its inner nature, and so, to its particular function in the overall process.(Nechyporchuk *et al.*, 2018)

Endoglucanases, also called endocellulases, hydrolyse amorphous regions of cellulose, whereas cellobiohydrolases, also called exoglucanases, are in charge of cleaving the endings of both crystalline or amorphous domains bringing about tetra-saccharides and di-saccharides, the latter being the hereinbefore mentioned cellobiose. Additionally, β-glucosidases, or also called cellobioses, hydrolyse the abovementioned products of exoglucanases catalysation into glucose. (Nechyporchuk *et al.*, 2018; Rol *et al.*, 2019)

Indeed, aftermaths such as the decrease in the degree of polymerization stems from exoglucanases performance, although in the other hand endoglucanases are regarded as the key enzymes since they will be able to avoid the decrease in the degree of polymerization and intensify CNFs defibrillation. (Nechyporchuk *et al.*, 2018; Rol *et al.*, 2019)

However, most of these enzymes could be irreversibly attached to lignin, unless this non-cellulosic materials are completely vanished, otherwise the process will not be as efficient as expected. (Nechyporchuk *et al.*, 2018; Rol *et al.*, 2019)

Functionalisation can be explained as a cutting-edge open-up yet optional section in the process of nanocellulose implementation. Specifically, functionalisation means to modify the surface of CNFs, which afterwards will render new capabilities and thus, new applications.(Abdul Khalil, Y Davoudpour, *et al.*, 2014; Mishra, Sabu and Tiwari, 2018)

In composite manufacture, nanocellulose surface modification successfully endeavour to bear with CNFs incompatibility with non-polar polymers mediums that lead to a non-scattered dispersions along with paltry interfacial adhesions with the hydrophobic matrix. (Abdul Khalil, Y Davoudpour, *et al.*, 2014; Mishra, Sabu and Tiwari, 2018)

2.2.3. CNFs functionalisation

Functionalisation may be classified as regard the nature of the modification intended to apply. Molecular functionalisation encompasses all those surface modification coating processes wherein a molecule is engrafted, or a chemical reaction is triggered to commonly catalyse the hydroxyl groups in another functional group required. (Mishra, Sabu and Tiwari, 2018)

Molecular functionalisation might be accomplished via surface modification through adsorption or molecular grafting. Adsorption, which is the simplest way to attempt surface amendments, aims to stick polyelectrolytes on CNFs surface to stir up repulsive forces that could overwhelm cohesion forces lead by hydrogen bonding networks. (Rol et al., 2019; Abdul Khalil, Y. Davoudpour, et al., 2014)

Chemical grafting of molecules is focused whether on the formation of ionic groups or the generation of hydrophobic surfaces. Formation of ionic groups, which targets similar purpose than that of polyelectrolytes, is carried through with sulfonation, carboxymethylation, as well as the afore-explained carboxylation. Generation of hydrophobic surfaces is carried out via acetylation, esterification and silylation.(Kalia et al., 2014; Rol et al., 2019; Abdul Khalil, Y. Davoudpour, et al., 2014)

Macromolecular functionalisation is achieved through polymer grafting. As proof, polymers which were used to fulfil this purpose are polyepoxides, polypropylene, polylactic acid as well as polyurethane, chitosan and polysulfone.(Mishra, Sabu and Tiwari, 2018)

Functionalisation with inorganic compounds constitute another strategy which intends for giving new properties to nanocellulose such as an improved electrical conductivity and so on to foster a wider application range for this nascent and novel material.(Abdul Khalil, Y. Davoudpour, et al., 2014; Mishra, Sabu and Tiwari, 2018)

2.2.3. CNFs applications

In 1983 the first sample of CNFs was prepared, thence immediately in 1995 appeared the first successful application of nanocellulose as reinforcing agent in composite manufacture.(Rajinipriya et al., 2018)

Thenceforth, an onward rush of applications came along with the continuous improvement in nanocellulose-related techniques involved in the extraction and conditioning of CNFs.

Albeit somewhat redundant, nanocellulose window of opportunities is getting even wider since this biopolymer is found wherever, in the wake of this, the idea of an industrialized production of this material have already been thoroughly considered, without thereby earth biomass integrity being put in jeopardy as nanocellulose weight ratio per gram of biomass is remarkable and many sources like industrial and agricultural waster are also available.(Rajinipriya et al., 2018)

One such example could be the presence of cellulose nanomaterials in water treatment technologies. Nanocellulose has been harnessed as contaminant adsorbent due to its low cost, omnipresence, great surface area-to-volume ratio as well as ease of surface functionalization, thereby this pioneering material is rivalling and trying to replace the mainstay of adsorptive media, which is the activated carbon.(Karim et al., 2016; Ummartyotin et al., 2017; Voisin et al., 2017)

Additionally, nanocellulose properties have been employed in the fabrication of membranes for water treatment. CNFs/polymer nanocomposites have been designed to serve in a broad range of membrane processes, namely hemodialysis, nanofiltration, ultrafiltration, microfiltration and so and so forth. (Karim et al., 2016; Ummartyotin et al., 2017; Voisin et al., 2017; Mahfoudhi and Boufi, 2017)

Moreover, hydrophilicity together with a supervised surface chemistry allows nanocellulose to dodge bio-fouling and organic fouling, which are common problems in membrane technology.(Karim et al., 2016; Ummartyotin et al., 2017; Voisin et al., 2017; Mahfoudhi and Boufi, 2017)

On top of that, cellulose nanomaterials have also been used towards stabilizing reactive nanoparticles intensifying, at the same time, sorption and degradation of target contaminants. In environmental remediation, nanocellulose spin-off aerogels with low density, outstanding surface area and great porosity are manufactured via supercritical drying process or freeze-drying technique adding surface functionalization with the view of enhancing heavy metal, oil adsorption, dyes adsorption and air contamination adsorption.(Karim et al., 2016; Ummartyotin et al., 2017; Voisin et al., 2017; Mahfoudhi and Boufi, 2017)

Furthermore, in municipal or industrial wastewater treatments, nanocellulose was utilized as a flocculant duly reducing water turbidity and enhancing sedimentation. Surface modification and conditioning aids to improve upon adsorption mechanisms intensifying flocculation activity. (Karim et al., 2016; Ummartyotin et al., 2017; Voisin et al., 2017; Mahfoudhi and Boufi, 2017)

Nanocellulose-based composites have already been touted as an affordable and sustainable new source of sensor materials. Gas detection sensors are clearly on the need to find a combination between semiconductor substance and conductive polymer. Bearing this in mind, nanocellulose could satisfy this demand by virtue of the fact that CNFs can be fused with a conductive polymer or that CNFs can be modified on the surface to became conductive by itself.(Ummartyotin and Manuspiya, 2015)

Nanocellulose have also been included as a potential host-matrix for moisture-sensing materials. The mainstay in humidity-sensing media is undoubtedly ceramics, yet this kind of materials are remarkably brittle.(Ummartyotin and Manuspiya, 2015)

Therefore, nanocellulose has been used as framework wherein ceramic nanoparticles can be attached onto the surface. This type of matrix renders more flexibility reducing brittleness and broadening the application range of this sort of sensors. Besides, nanocellulose can also be blended with an organic conducting polymers providing not only enhanced mechanical properties but also intensified sensing abilities and improved thermal resistance.(Ummartyotin and Manuspiya, 2015)

Nanocellulose has also spawned a huge variety of chances in the packaging industry since petroleum-based waste contamination have raised awareness within worldwide population in order to substitute this environmentally non-friendly materials for renewable and biodegradable ones.(Azeredo, Rosa and Mattoso, 2017; Ferrer, Pal and Hubbe, 2017; Hubbe et al., 2017)

By way of example, active food packaging systems exhibit functional properties that enables not only a passive protection of food products, but also a active improvement in food quality via dissemination of active compounds like antifungal and antimicrobial agents onto food surface. (Azeredo, Rosa and Mattoso, 2017; Ferrer, Pal and Hubbe, 2017; Hubbe et al., 2017)

With the view to improve upon shelf life of food products, evade the escape of food stinks and avoid the accumulation of undesirable odors, nanocellulose-related films were conceived as powerful barrier layers that successfully hinder oxygen permeation through packaging material.(Azeredo, Rosa and Mattoso, 2017; Ferrer, Pal and Hubbe, 2017; Hubbe et al., 2017)

Nanocellulose, cannot be considered as a compostable material, though it could be if the specimen is tiny and thin enough to be degraded in six months. However, biodegradability of nanocellulose is quite remarkable due to its nano-scaled dimension which offers a huge superficial area proffering abundant catalytic sites. In addition, the fact of being a natural-occurring polymer means to say that many organisms are able to degrade it.(Azeredo, Rosa and Mattoso, 2017; Ferrer, Pal and Hubbe, 2017; Hubbe et al., 2017)

Despite all these noticeable properties, all nanocellulosic materials share a common weak point. It is known beforehand that cellulose exhibit a hydrophilic nature, which provides great hindrances in terms of water and vapour barrier performance. Water permeance is still the foremost challenge in material packaging research and in composite manufacture as well, in view of the fact that moisture presence, or even worse, water presence may provoke fibre-swelling and fibre-shrinkage afterwards leading to a poor matrix-fibre interaction. (Azeredo, Rosa and Mattoso, 2017; Ferrer, Pal and Hubbe, 2017; Hubbe et al., 2017)

A part from this, (Du et al., 2017) reported nanocellulose feasibility in energy devices and novel applications as conductive materials. In practice, this report deals with nanocellulose based supercapacitors, nanocellulose based lithium-ion batteries as well as nanocellulose usage in electrodes, as separators and as electrolytes. It is also mentioned the most likely existence of solar cells machined with nanocellulose.

This comes down to say that nanocellulose applications can be found in the most unexpected technological fields, therefor nanocellulose may be comparable with those so-often-used synthetic only carbon-based and nano-scaled platelets of graphene and by-products thereof.

In the biomedical healthcare industry, nanocellulose plays an active role on account of its biological properties. Firstly, nanocellulose spin-off products are considered to be biocompatible, despite having stirred up moderate foreign body responses in vivo. Thereby, nanocellulose-derived materials may be able to coexist with the human tissue without any deleterious changes being occurred in the body therefor.(Lin and Dufresne, 2014; Halib et al., 2017)

Nonetheless, one should highlight that animal tissue lacks the ability to degrade cellulose, which may suppose a kind of shortcoming. In spite of this, nanocellulose spin-off biomedical products, namely TEMPO-CNFs have proved hemocompatibility, which is a useful trait considering the design of blood-touching surfaces or synthetic organs.(Lin and Dufresne, 2014; Halib et al., 2017)

Nanocellulose biomedical by-products are being applied from micro and molecular scale to a macroscopic level, though new strategies and frontiers are awaiting to be discovered.

At the molecular level, tissue bio-scaffolds for cellular culture were conceived to generate a rather more cell friendly environment to stimulate cell proliferation by virtue of nanocellulose mechanical properties and biocompatibility. Nanocellulose-based bio-scaffolds exhibit numerous shapes and forms made up of by-products thereof such as aerogels, electrospun nanofibers, hydrogels, composites and membranes. (Lin and Dufresne, 2014; Halib et al., 2017)

In advanced drug-loaded systems, nanocellulose is involved in terms of advanced excipient capable of condensing even more the aforementioned systems, as well as exceptional drug carrier enabled to keep rationing the drug for longer than other conventional ones.

Additionally, nanocellulose spin-off drug carriers can be classified into microspheres, hydrogels and membranes according to the form displayed. (Lin and Dufresne, 2014; Halib et al., 2017)

Nanocellulose has also been chosen as an optimal candidate for carrier in enzyme/substrate complex immobilization. This method is an oftentimes technique that endeavour to solve enzyme catalytic failure and instability occurring all along the storage and operating periods which stems from irreversible enzyme or substrate aggregation, unfolding and autolysis. (Lin and Dufresne, 2014; Halib et al., 2017)

Biocompatibility and non-toxicity allow nanocellulose to be harnessed duly in this sense, since this material may intensify enzyme/substrate stability, activity and loading at any time. (Lin and Dufresne, 2014; Halib et al., 2017)

Furthermore, nanocellulose surface shows innumerable hydroxyl groups is case of opting for an electrostatic adsorption as immobilizing strategy, although other entrapment techniques can also be applied. (Lin and Dufresne, 2014; Halib et al., 2017)

Apart from physical adsorption strategies, chemical binding also might be a suitable option, yet slightly more complicated and expensive. In spite of this, nanocellulose conditioning might endow nanocellulose with the binding sites required for any kind of chemical linkage with whichever sort of enzyme. This strategy provide the enzyme/substrate complex with more stability and outstanding enzyme/substrate loading.(Lin and Dufresne, 2014; Halib et al., 2017)

Nanocellulose and its remarkable biomechanical properties have encouraged the investigation, development and exploitation thereof, as well as the employ of this material spin-off products as tamper-proof replacement biomaterials.

One instance could be the blood vessel replacement done in mostly cases to properly irrigate the myocardium when a cardiovascular disease appears. This operation is called coronary bypass graft surgery and nanocellulose is about to become the most suitable material for being not only biocompatible but also hemocompatible and for exhibiting great toughness and no signals of thrombogenicity.(Lin and Dufresne, 2014; Halib et al., 2017)

Another example might be nanocellulose bio-mimesis with structural soft tissues such as ligaments, meniscus and cartilages. Nanocellulose is enabled to play the same role than this afore-revealed soft tissues due to a low degree of calcification, great shelf life and similar mechanical features than that of the aforementioned soft tissues.(Lin and Dufresne, 2014; Halib et al., 2017)

Additionally, in (Lin and Dufresne, 2014) it has been demonstrated nanocellulose intervention in form of biocomposite hydrogel as nucleus pulposus replacement to be feasible. Nucleus pulposus is the gelatinous matter placed bwetween two vertebral bodies, in the center of the invertebral disk. The abovementioned biocomposite hydrogel became a proper material to restore damaged invertebral disk as withstands on the basis of great fatigue resistance, suitable swelling ratio, similar relaxation properties and paltry strain.

Despite being at the fundamental stage, nanocellulose has also been harnessed as an advanced nanomaterial for tissue repair, regeneration and healing, as for instance, in terms of skin tissue repair and wound healing or bone tissue regeneration and healing. (Lin and Dufresne, 2014; Halib et al., 2017)

Nanocellulose have also made name for itself in the food industry. In (Gómez H. et al., 2016) is reported the use of nanocellulose as a natural stabilizer and emulsifier in some food products such as puddings, toppings, soups and so on and so forth.

Nanocellulose has recently been regarded as an interesting replacement for those conventional emulsifying and stabilizing agents since it brings related organoleptic properties like consistency and unctuousness. (Gómez H. et al., 2016)

The aim of using nanocellulose in such foodstuff is to reduce the amount of fats involved in the process, and so to obtain a low-fat formulation. (Gómez H. et al., 2016)

Furthermore, in view of the attributes like crispiness, great palatability and accurate texture, nanocellulose has started to be considered as one more functional ingredient. Nanocellulose could be utilized as a dietary fibre supplier since cellulose is known beforehand to render countless health benefits such as the reduction of cardiovascular disease and obesity risk, as well as laxation and blood cholesterol lowering. (Gómez H. et al., 2016)

3. Experimental plan

In this section, the experimental procedure chosen, and the materials harnessed to accomplish the objectives of this thesis are going to be duly itemized. The experimental procedure explanation will be classified in two parts: preparation of the nanocomposite and characterization of the nanocomposite. In the first rank, methods and techniques applied to achieve a seamless and scattered integration of CNFs into the PMMA plastic matrix are going to be explained. In the other rank, several thermomechanical analyses to which the nanocomposite had to be undergone are going to be briefly described.

3.1. Materials

3.1.1. Poly-Methyl Methacrylate

PMMA V8257 Altuglass® provided by the research group CELLMAT from the University of Valladolid in form of pellets.

3.1.2. Cellulose Nanofibres

Hydrogel with a weight percentage of CNFs equivalent to 1% was procured by the University of Girona. This CNFs, which were isolated from *Eucaliptus globulus* dried and bleached pulp, exhibit the propertied displayed in table 2 shown beneath.(Serra et al., 2017)

Table 2. Summary of properties of CNFs.

Carboxylic Content (mmol/g CNF)		Degree of Polymerization (n)	Yield of fibrillation (%)
Methylene blue method	Conductivity method		
1.157	1.271	229	97.69±0.1

Transmittance at 600 nm (%)	Specific surface (m^2/g)	Diameter (nm)	Source
80	285,9	8,75	(Serra et al., 2017)

CNFs that were utilized in this thesis underwent a 10 mmol NaClO TEMPO carboxylation which result in the carboxylic contents set out in table 2. Methylene blue method and conductivity method are different paths to obtain a value of carboxylic content. In both cases, the carboxylic content comes down to say there are existing approximately 5 glucopyranose units per molecule of carboxyl, which is a remarkable quantity.

Because of this, CNFs mild aqueous dispersion display clearness and transparency. In the wake of this, inasmuch as the carboxyl content rise the clearer will be the solution.

Moreover, an outstanding yield of fibrillation lead to thin fibres that renders a huge surface area.

In addition, this huge degree of polymerization demonstrates that the fact of displaying such carboxyl content avoids an excessive implication of any kind of mechanical treatment, otherwise if the mechanical treatment is the only strategy developed to bring about the intended defibrillation the degree of polymerization may would be drastically reduced.

3.1.3. Dimethylformamide

N, N-dimethyl-methanamide 99% pure, also called Dimethylformamide (DMF) is an organic aprotic solvent utilized to hold the PMMA and the CNFs in the same dispersion.

3.2. Experimental procedures

With the purpose of assessing the effect of a structured framework of CNFs embedded in the PMMA plastic upon the thermal and mechanical properties of the resulting nanocomposite, diverse nanocomposites with 0%, 0.5%, 1%, 2% and 3% of weight percentage of CNFs were manufactured.

3.2.1. Preparation of the nanocomposite

The main purpose of this experimental part is to blend PMMA plastic and CNFs in order to obtain a scattered PMMA/CNFs thin layer.

3.2.1.1. Preparation of the master batches

The maximum weight percentage of CNFs feasible to be dispersed in DMF without any kind reverse coalescence is 0,3 wt% and 40% is the maximum concentration of PMMA able to be dissolved in 100 g of DMF. As a result of this, the maximum weight of every single abovementioned sort of nanocomposite was 10g. In the wake of this, the experimental description will be performed as if only 10 g of each type of nanocomposite blend were done.

Firstly, 66.1 g of 1 wt% CNF hydrogel is diluted in 152,9 g of distilled water in order to obtain 219 g hydrogel master batch at 0.3 wt% that will contain the mass of CNFs enough to produce 10 g of each kind of nanocomposite blend. In order to seek a scattered dispersion from the beginning of the process, the recently made dissolution undergone a ultrasonication process under the Sonic Dismembrator Model 705 Fisher Scientific™ at 100% of amplitude, 100 watts of power and for 15-20 minutes.

While this ultrasonication is being carried on, the temperature of the dispersion will rise due to the energy provided by the ultrasonicator. Therefore, the temperature was diminished from time to time in order to avoid the hydrogel to reach a high temperature that could damage the CNFs.

Meanwhile, 55 g of neat PMMA may be dissolved in 137.5 g of DMF by using magnetic stirring at 120ºC under a fume hood since DMF is considered to be potentially hazardous for health.

Around the Tg, PMMA starts to exhibit an increased viscoelastic behavioural pattern that eases this very same plastic to be dissolved. In spite of this, huge amounts of organic solvent evaporated which provoked the dispersion to became even more dense. With the aim of avoiding this, DMF content should had to be replenished periodically. Despite the fact that only 50 g of neat PMMA are on the need in order to obtain 10 g of each type of nanocomposite, it is recommended to add a margin as PMMA 40 wt% solution is remarkably dense, and part of this very same plastic will remain attached to the vessel wall when this is poured.

3.2.1.2. Solvent Exchange method

As soon as the master batch 0.3 wt% hydrogel display a clearer look, 219 g of DMF had to be carefully dropped in the dispersion with magnetic stirring assisting and a solvent exchange method should be performed in order to dispose of all the water content and spawn a CNFs/DMF dispersion enable to be merged with a PMMA/DMF solution without CNF aggregation occurring.

The reason behind this process suitability lays in the properties of the solvent selected. DMF is a polar aprotic organic solvent which means that can accept a proton and therefore to stablish a hydrogen bond, but it is unable to donate a proton since no hydrogen atom is present within its inner chemical structure, which means that it cannot spawn any hydrogen bond by itself.

This come down to say that DMF is able to generate weak hydrogen bonds with water and with PMMA which makes this solvent miscible with water and capable of dissolving PMMA at the same time.

Unlike DMF, a water molecule can accept and donate protons doubly. Hence, the likelihood of CNFs reverse coalescence in water presence is higher since this is capable of triggering the activation of more hydrogen bonds than in DMF only presence.

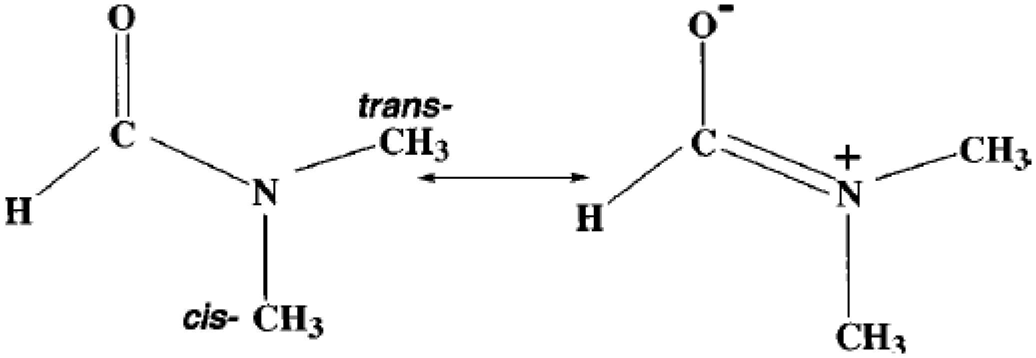

Figure 6. Dimethylformamide resonance structures.(Forde, 1999)

Moreover, as set out in figure 6, DMF is an organic amide that displays a resonance structure wherein the right-hand form is the only one capable of accepting a proton since the carbonyl carbon exhibit a negative charge.

However, all the possible hydrogen bonds that this negative-charged carbonyl carbon could create with CNFs surface hydroxyl groups will be weaker than those of water as the presence of positive-charged nitrogen atom nearby will debilitate the intensity of this very same hydrogen bonds.

In addition to that, the fact of exhibiting a resonance structure means to say the electronegativity of the carbonyl carbon will not be exactly constant since in a resonance structure both kinds of forms coexist at the same time within the molecule.

As a result of this, DMF does not only ease CNFs scattering but also reduces the risk of CNFs self-aggregation phenomena and enable CNFs to be embedded as an entangled yet percolated particle distribution within the PMMA matrix. In the wake of this, water content had to be removed from the CNFs dispersion through a solvent exchange method.

The solvent exchange method is defined as a liquid-liquid separation through which a solution switch from one solvent to another without been dried at any moment.

This method is based on distillation technique that endeavour to separate a mixture of solvents by making use of selective boiling and condensation points. However, a simple distillation might not be a suitable option since the temperature needed to evaporate the water may be slightly able to damage the fibres.

As a result of this, vacuum distillation was the technique carried out to perform the solvent exchange process. Vacuum distillation technique intends to reduce the pressure in order to achieve a higher water evaporation rate at a lower temperature.

In order to accomplish this solvent switching process, a BÜCHI™ Rotavapor R-200 was harnessed with water boiling bath at 80ºC and at 12 mBa of vacuum with a membrane pump Vacuubrand® 6962 44 MZ2C for 40 minutes. In order to assure a proper water removal, the weight of the condensed water had to be equivalent to the initial water content which was 218.34 g.

Once the distillation process came to an end, DMF content had to be replenished as some organic solvent might be evaporated during the procedure. Afterward, CNFs/DMF dispersion had to undergo another ultrasonication process for 10 minutes since some CNFs aggregations were noticed.

In order to make sure that no fibre losing had occurred during the process, 2 g of the DMF/CNFs master batch were dry-weighted. Subsequently, the hereinbefore mentioned types of nanocomposites were prepared by blending the 0.3 wt% DMF/CNFs master batch and the 40 wt% DMF/PMMA master batch in different proportions, as set out in the table below.

Table 3. Blend proportion for each type of nanocomposite.

Blend proportion	40 wt% PMMA/DMF (g)	PMMA (g)	0.3 wt% CNF/DMF (g)	CNF (g)
0 wt%	35	10,00	0	0,000
0.5 wt%	34,83	9,95	16,56	0,050
1 wt%	34,65	9,90	33,13	0,099
2 wt%	34,3	9,80	66,26	0,199
3 wt%	33,95	9,70	99,39	0,298

Despite the continuous ultrasonication assisting aided the dispersion of the CNFs in every step of the process, reverse coalescence phenomena appeared in those nanocomposite blends whose weight percentage of CNFs were high enough. Namely, 2 wt% and 3 wt % nanocomposite blends needed to undergo a ultrasonication treatment under the Homogenizer CY-500 Optic Ivymen System ® at 100% of amplitude, 100 watts for 40 minutes approximately. Once this was achieved, every single nanocomposite blend was cast in a petri dish and left desiccating for 48 h at room temperature in order to remove all the organic solvent.

3.2.1.3. Casting/Evaporating technique

With the aim of preparing PMMA/CNFs nanocomposite film, casting/evaporating technique was applied.

In this technique, the sample undergoes a solvent-evaporating process with the aid of a vacuum oven. The vacuum is highly needed again as DMF vapor pressure at atmospheric pressure is lower than that of water and the samples should not be subjected to temperatures above 80ºC otherwise, CNFs physical integrity could be jeopardized.

This slow process allows for the CNFs to interact with each other and with the PMMA matrix for longer than other manufacturing processes. This fact gives rise to enriched interplay among CNFs and between the PMMA matrix and the CNFs which results in more presence of hydrogen bonds.

A squared silicon mould of 65 cm^2 was chosen to cast each of the samples. The mould needed to be made of silicone since every time PMMA achieves a solid state when the solvent has completely evaporated some kind of void makes this very same PMMA film to be incredibly attached to the base of the mould.

As a result of this and with an eye on avoiding a PMMA sticking layer at the base of the mould, a silicone mould was chosen since this material enables a certain degree of malleability that allows for the air to seep through the bottom of the mould and the PMMA layer making easier and more feasible PMMA detachment from the mould.

Considering that 1.19 g/cm^3 is the density of the PMMA, it was intended to spawn a 1mm thick layer of each kind of nanocomposite. In order to accomplish this goal, 7.74 g of each sort of nanocomposite were re-dissolved in 100 g of DMF and cast in several of these afore-said squared silicone moulds which were later put into the vacuum oven Vacutherm Heraeus Instruments®.

Before applying any heat, a vacuum of 1 Ba was performed with the hereinbefore mentioned membrane pump for 2 min in order to make implode all the bubbles that could be remaining in the samples. Once this was done, the samples spent 95 h at 70ºC and at a vacuum of 0.6 mBa. A vacuum solvent trap condenser glass was placed between the vacuum oven and the membrane pump so as to avoid DMF volatile fumes to enter the membrane pump.

Consequently, the pressure inside the oven increases progressively inasmuch as the solvent evaporates. As a result of this, twice a day the volatile solvent was removed by means of the membrane pump and then replenished with outside air in order to avoid massive accumulation and therefore condensation of DMF inside the oven which could hamper the drying process.

The obtained samples were called CNF-0%; CNF-0.5%; CNF-1%; CNF-2% and CNF-3% in accordance with the weight percentage of CNFs.

3.2.2. Characterization of the nanocomposite

In this section, the main purpose encompasses the mechanical evaluation of each sort of nanocomposite by means of a tensile test, the optical evaluation via transmittance measurement and the observation of each kind of nanocomposite to determine their scattering level and their overall appearance.

3.2.2.1. PMMA/CNFs nanocomposite Observation

PMMA/CNFs nanocomposite observation may give us an idea of how these very same fibres have been distributed all along the PMMA matrix. In order to accomplish this a polarized-light microscope JENAVAL® was used with a digital camera EUROMEX® and a plan-achromat objective Carl Zeiss Jena®.

The use of a polarizer allows for taking more defined and clearer pictures of the CNFs since this fibres exhibit birefringence phenomenon due to cellulose nanocrystals within its inner structure.

3.2.2.2. Optical Characterization

3.2.2.2.1. Transmittance

The optical characterization meant to gauge the transmittance of each kind of nanocomposite at different wavelengths among de UV-Visible spectrum by means of a UV-Visible spectrophotometer UV-1700 Pharma Spec Shimadzu®.

The wavelengths at which the transmittance of each kind of nanocomposite was measured are shown in the table below.

Table 4. UV-Visible spectrum wavelengths.

Description	Wavelength (nm)
λ_1	380
λ_2	475
λ_3	495
λ_4	570
λ_5	590
λ_6	620
λ_7	750

3.2.2.3. Mechanical Characterization

3.2.2.3.1. Tensile test

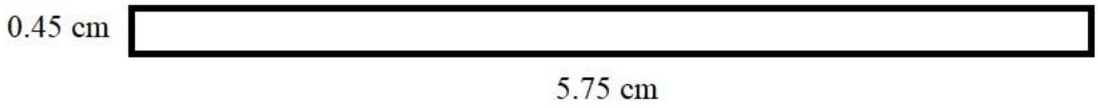

Figure 7. Picture of the size and the form of the specimen utilized to perform the tensile test.

The test specimens, as it may be noticed in figure 7, were obtained by heating up each type of nanocomposite film up to 85ºC in order to lessen the rigidity of these films eluding any kind of breakage occurring.

Once those displayed a rubber-like behaviour, it was proceeded to cut 10 specimen tests for each sort of nanocomposite, which means that a total of 50 test specimens were cut.

Table 5. Thickness of every type of test specimen in accordance with each kind of nanocomposite.

Thickness (mm)	1	2	3	4	5	6	7	8	9	10	Average (mm)
CNF-0%	1,26	1,23	1,14	0,72	0,78	1,18	0,71	0,80	0,85	0,79	0,94
CNF-0.5%	0,97	0,99	0,95	0,97	0,93	0,97	1,02	1,05	1,02	0,95	0,98
CNF-1%	1,05	0,70	1,00	0,92	0,97	0,88	0,78	1,04	0,89	0,80	0,90
CNF-2%	0,86	0,99	0,86	0,97	1,00	0,95	0,88	0,89	0,87	0,92	0,92
CNF-3%	0,92	0,95	0,82	0,83	0,93	0,79	0,85	0,80	0,83	0,89	0,86

The tensile test was performed by means of texture analyser TA.XT.plus® at a test speed of 10 mm/min and a break sensitivity of 0,196 N. The distance at which the tensile test was performed ranged from 5 mm to 10 mm. The thickness of each test specimen, as it is set out in table 3, was determined by using a micrometre.

Young’s modulus, ultimate tensile strength as well as the tensile toughness and the strain at failure were the mechanical parameters chosen to gauge the mechanical properties of each kind of nanocomposite. The calculation of these was applied to the most representative data discarding those samples that were not duly clamped to the texture analyser or that displayed some kind of notch or flaw within the test specimen.

Based on the data of force and displacement given by the texture analyser, it was calculated the stress (σ) by dividing the force by the cross-sectional area of the test specimen, as set out in the formula below.

$$\sigma(Pa) = \frac{F(N)}{A(m^2)} \qquad (1)$$

The strain at failure (Ɛ) was calculated dividing the given displacement by the 20 mm gauge length, as it is show in the formula below.

$$\varepsilon = \frac{\Delta l(mm)}{l_0(mm)} \tag{2}$$

The ultimate tensile strength is defined as the maximum value of stress.

Young's modulus was calculated by dividing the stress (σ) between the strain (ε) as it is shown in the formula below.

$$E(Pa) = \frac{\sigma(Pa)}{\varepsilon} \tag{3}$$

Finally, the tensile toughness was calculated by obtaining the area under the stress-strain curve up to the maximum stress value.

4. Results and discussion

4.3. PMMA/CNFs nanocomposite Observation

As expected from CNF-0% nanocomposite, which is basically a neat PMMA film, no kind of fibre was found in any of the pictures taken under the PLM.

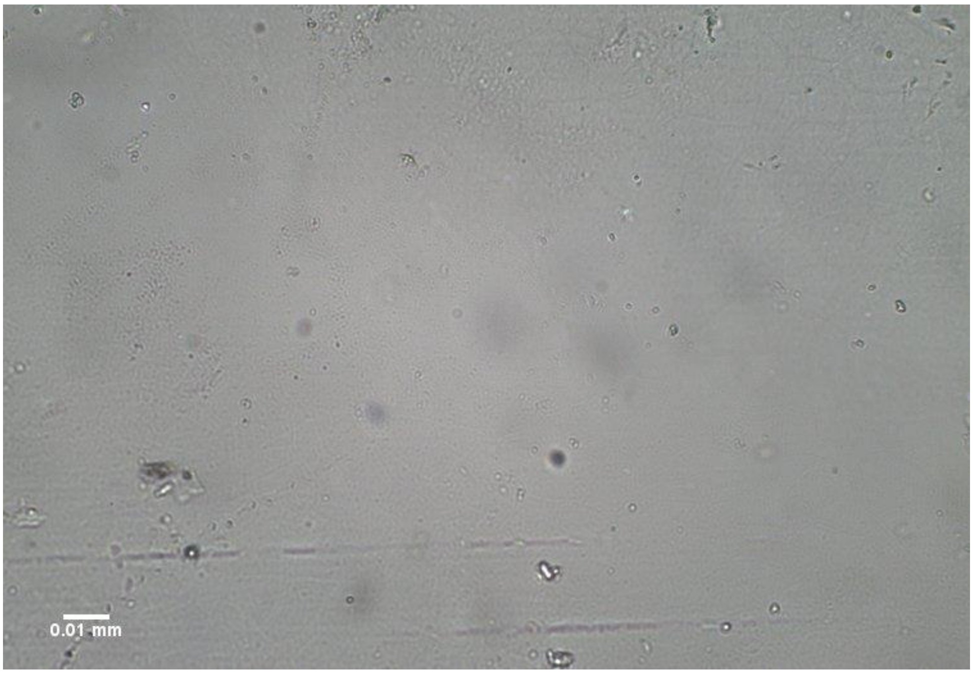

Figure 8. PLM picture of CNF-0% nanocomposite film at 31,25 magnifications.

In the figure 8, it can be noticed that may some sort of impurities or PMMA agglomerations are present within the matrix as a result of the dissolving process.

Despite that and after examining some of the provided pellets of PMMA, it was found that some of this once-considered contamination might be just part of the composition of the material since the same spots can also be observed in figure 9.

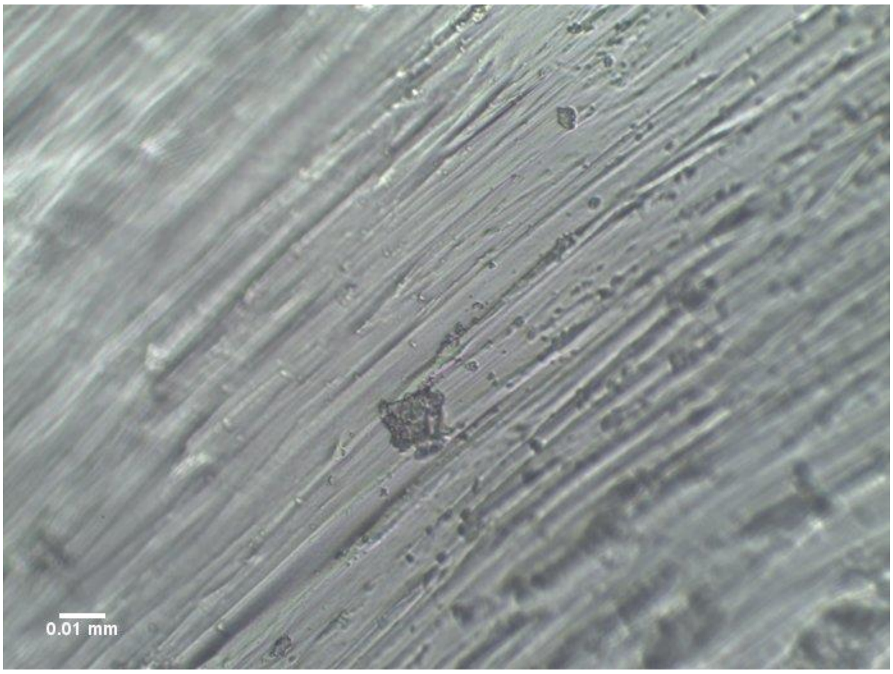

Figure 9. PLM picture of a PMMA pellet at 31,25 magnifications.

Prior to taking a deep look to CNF-0.5% film, 1 wt% CNF hydrogel was put under PLM observation with the aim visualizing the CNFs at first glance as this could help to make an idea of what they might aesthetically look like.

Figure 10. Picture of 1wt% hydrogel displaying CNFs appearance at 15,625 magnifications.

In figure10, it can be noticed some kind of rod-like transparent yet glowing structures that are sprawled all over the hydrogel. Those might be considered to be the CNFs. As it may be noticed, the length, the form and the manner in which each kind of fibre is set out in the space is completely different from each other. The only aspect they all have in common is the nanometric width.

Once the CNF-0.5% film was put under PLM observation, some CNFs were able to be sighted, as it is shown in figure 11 and 12.

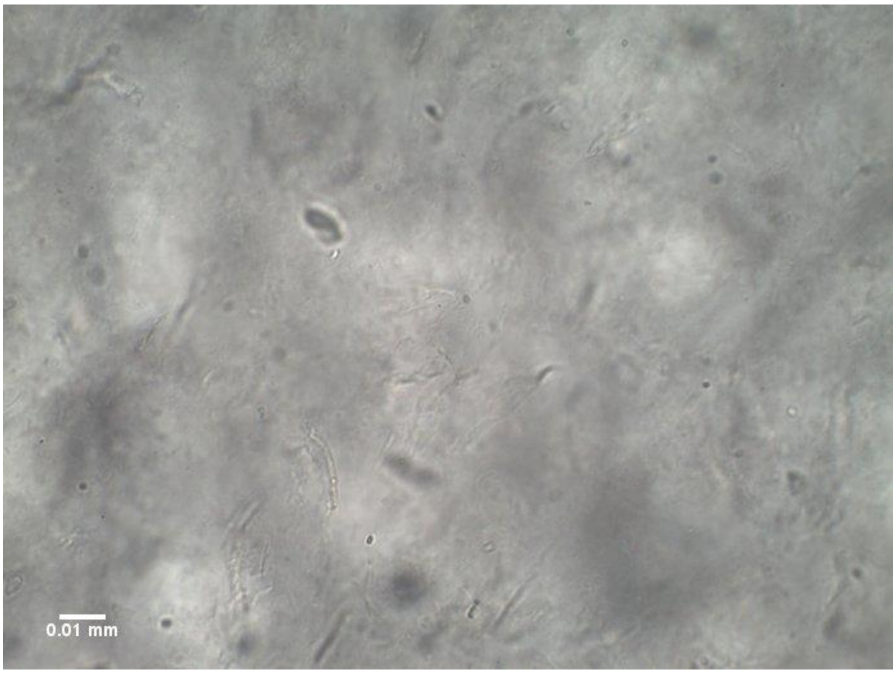

Figure 11. PLM picture of CNF-0.5% film at 31,25 magnifications.

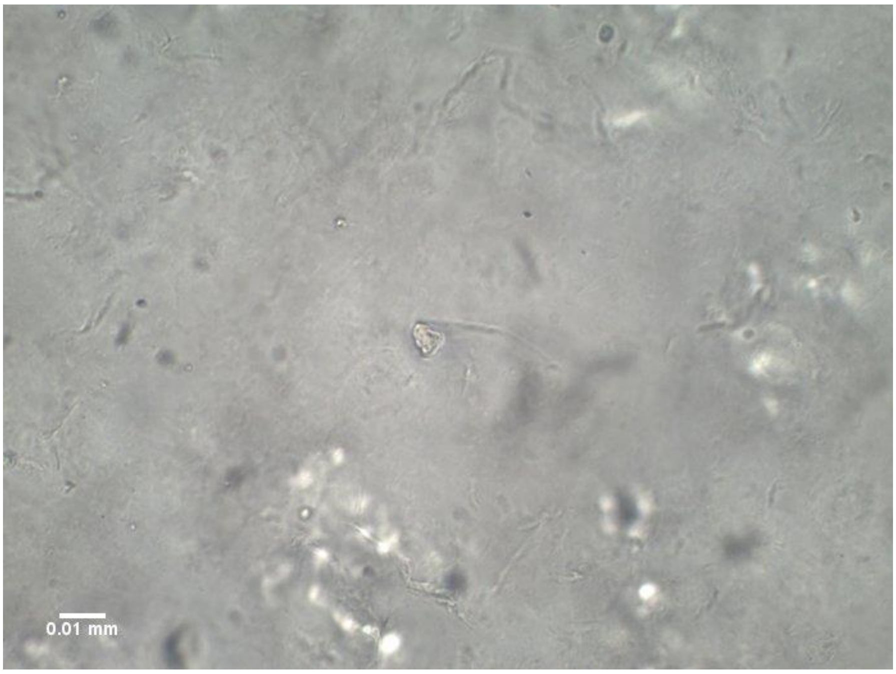

Figure 12. PLM picture of CNF-0.5% film at 31,25 magnifications.

Despite having observed punctually observed isolated CNFs, no percolated framework structure can be spotted as the CNFs content is not enough for such conformation.

Whilst CNF-0.5% PLM pictures show a common PMMA matrix background spotted with some isolated CNFs that may not provide a mechanical improvement, in CNF-1% PLM pictures randomly structured network can be noticed, as it is portrayed in figure 13 and 14.

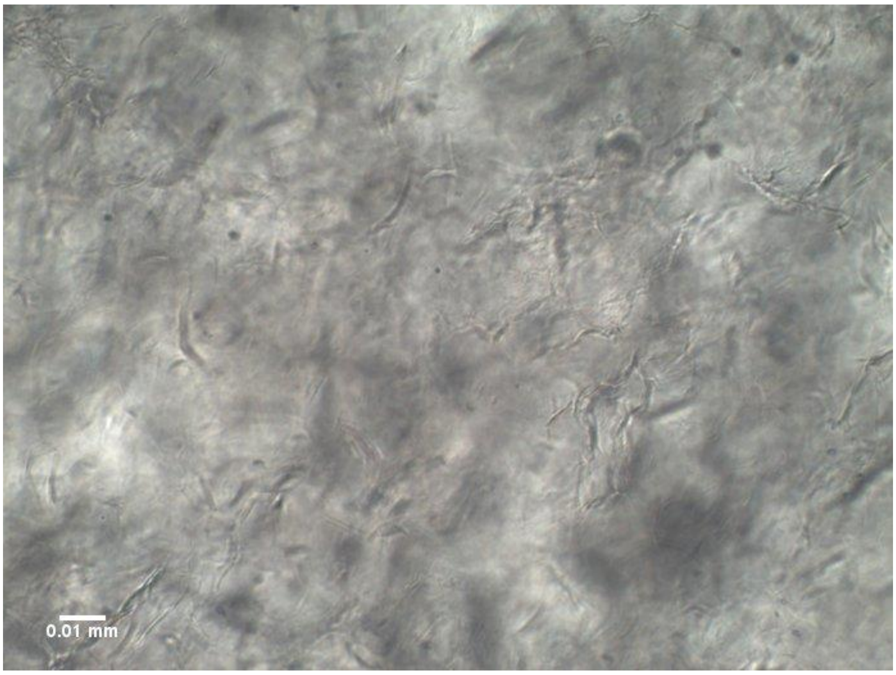

Figure 13. PLM picture of CNF-1% film at 31,25 magnifications.

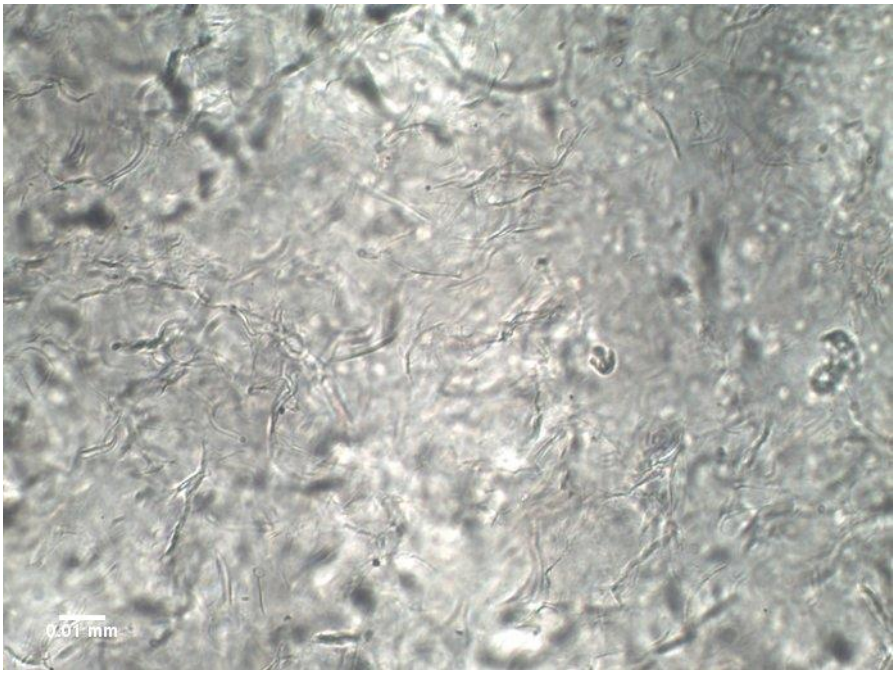

Figure 14. PLM picture of CNF-1% film at 31,25 magnifications.

CNF-1% PLM images clearly shown some kind of possible interplay between CNFs as the content of these is high enough to find themselves adjoining in the PMMA matrix. In spite of this, reverse coalescence phenomena might not be discarded at all since some fibres shown some sort of interwoven aggregations. In this case, the remarkable number of CNFs began to alter the PMMA matrix itself, which was no longer smooth at all.

Meanwhile CNF-1% exhibit a slight version of a randomly structured framework, CNF-2% actually displayed a richer distribution of CNFs, as it is set out in figure 15 and 16.

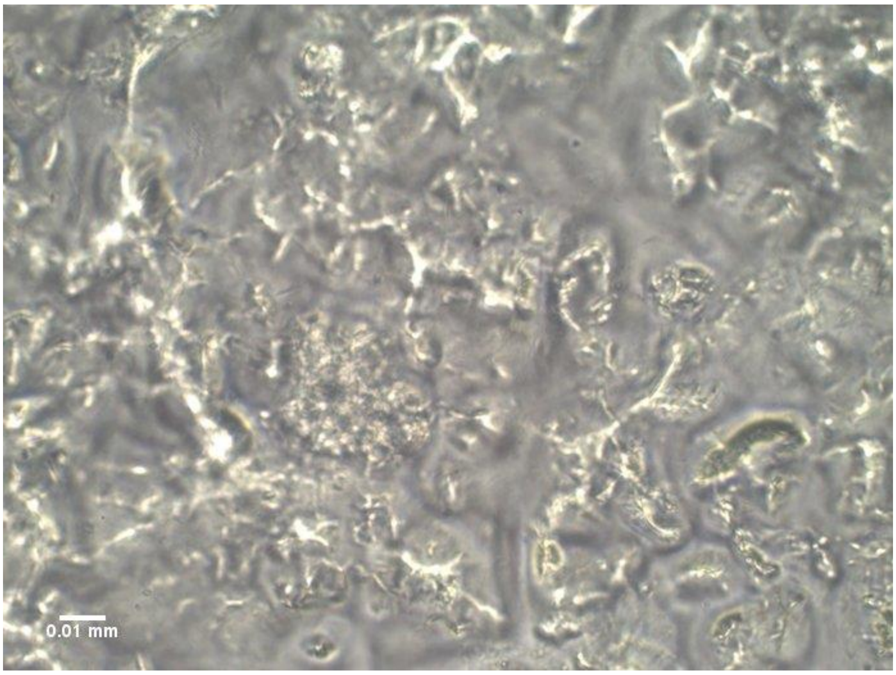

Figure 15. PLM picture of CNF-2% film at 31,25 magnifications.

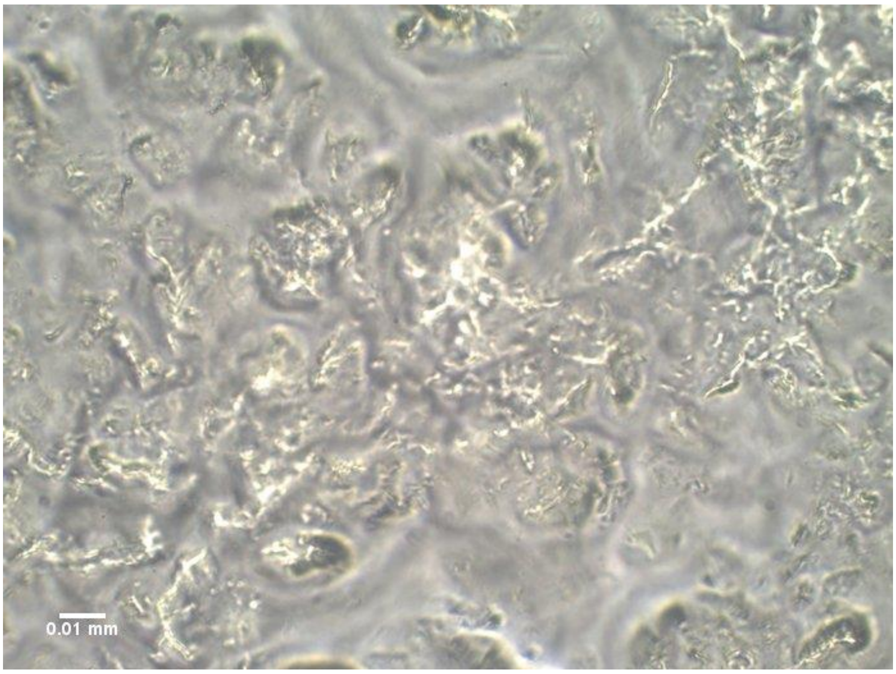

Figure 16. PLM picture of CNF-2% film at 31,25 magnifications.

In CNF-3% film pictures set out in figures 17 and 18, it might be observed an intensified interaction among the CNFs and the matrix. On top of that, in both types of films, CNF-2% and CNF-3% exhibit clusters of fibres wherein some kind coiling-like aggregations might be appearing. This may reinforce the CNF-CNF interplay providing improved mechanical properties to the nanocomposite. Even though, not all the fibres exhibit this spatial layout since many of them are straggly spread all over the matrix improving upon CNF-PMMA interaction, which also may aid to reinforce the mechanical properties of the nanocomposite.

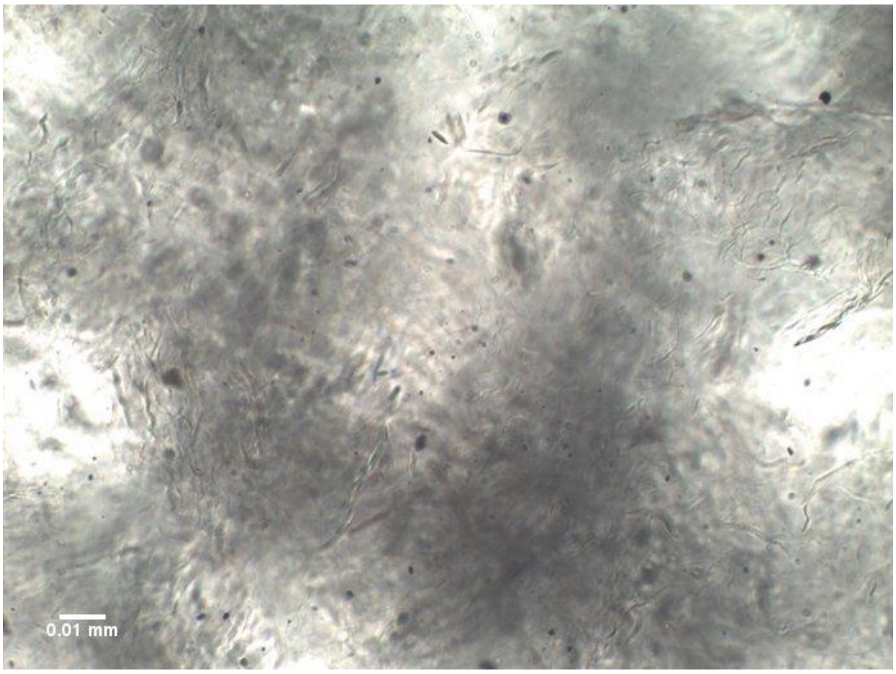

Figure 18. PLM picture of CNF-3% film at 31,25 magnifications.

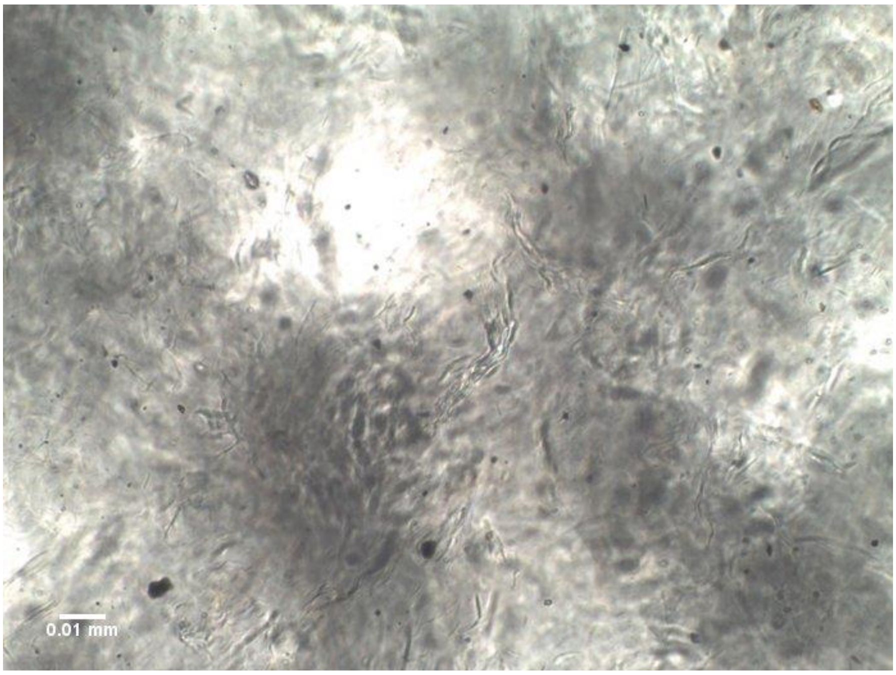

Figure 17. PLM picture of CNF-3% film at 31,25 magnifications.

4.2. Transmittance

Figure 19. Picture of each kind of nanocomposite in accordance with its CNFs content.

In figure 19 it can be noticed that CNF-0%, CNF-0.5%, and CNF-1% display a greater clarity and definition than CNF-2% and CNF-3%, which might be on account of the upward content of CNFs.

Apart from that, it may also be spotted in the same figure some kind of brownish nuance in the films belonging to CNF-2% and CNF-3% as meaning that inasmuch as the weight percentage of CNFs rise the greater will be the intensity of this brownish-like background colour.

Despite it may not be appreciated, CNF-1%, CNF-2%, and CNF-3% exhibit a fine-grained rougher surface than CNF-0.5% and CNF-0, which are really smooth. This fact might stem from the weight percentage of CNFs, since the higher the content of CNFs was the more noticeable also was the gelatinous rheological behaviour of the nanocomposite solution.

The number of CNFs might affect the rheological properties of the nanocomposite which later have an effect upon the dispersion of the blend poured in the silicone mould. This fact could be the reason behind the rough surface occurring traits of those aforementioned types of nanocomposites.

The outstanding surface area of the CNFs may render a thixotropic nature to those nanocomposite solutions wherein the CNFs content was high enough, as for instance CNF-1%, CNF-2% and CNF-3%. Thixotropy prompt the appearing of numerous little transparent bulky structures that avoid the proper homogeneously distribution of the nanocomposite blend along the silicone mould.

These afore-revealed bulky agglomerations, that slightly emerged from the surface of the nanocomposite mix, were the reason behind the grainy surface noticed in the hereinbefore mentioned kind of nanocomposites when the organic solvent had completely evaporated.

Thus, it is well known that the higher the CNFs content is, the lower will result the transmittance of the nanocomposite. Even though, unawareness arises when it comes to determining which of the numerous wavelengths that are comprised within UV-Visible spectrum will provide the higher or the lower transmittance for each kind of nanocomposite.

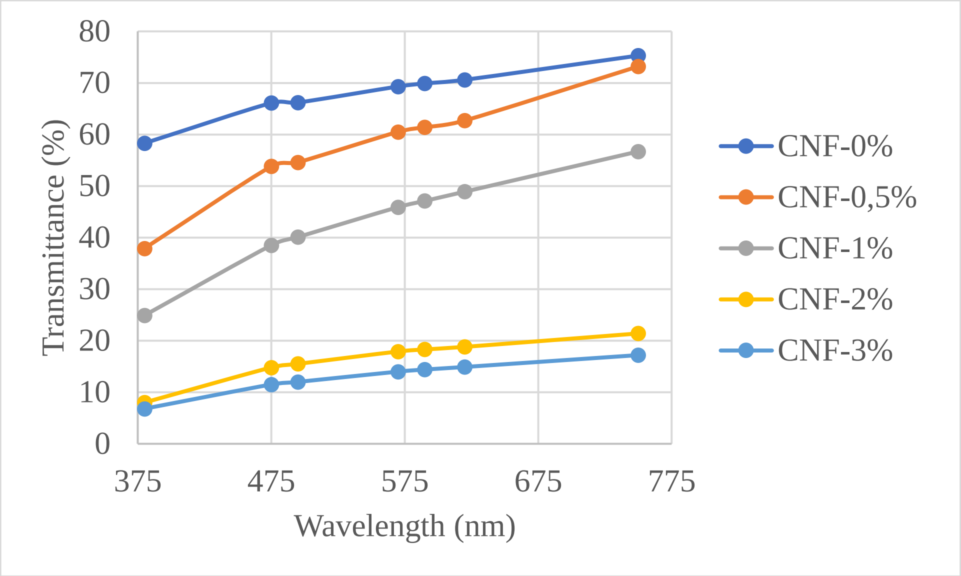

Figure 20. Transmittance of each type of nanocomposite with regard to UV-Visible spectrum.

Figure 20 clearly confirm the aforementioned assumption wherein the greater the CNFs content, the lesser will be the transmittance of the nanocomposite.

However, it might be spotted a noticeable difference in terms of transmittance between CNF-2% and CNF-3% as regard the rest of the nanocomposites that may also be noticed in figure 19. As mentioned recently, CNF-2% and CNF-3% clearly exhibit a translucid nuance rather than a clear and transparent film unlike the other types of nanocomposites.

It can also be observed the fact that all kinds of nanocomposites are prone to absorb those wavelengths which lean towards the UV spectrum. This optical feature is one of the main reasons behind the utilization of PMMA as a replacement of glass in many applications. This optical property might be even improved by the presence of CNFs, though this assumption could not be stated considering the experiment carried out.

In case of willing to prove the aforementioned observation, a UV absorbance measurement should be conducted.

4.3. Tensile test

The stress-strain curves corresponding to each type of nanocomposite that are hereinafter displayed, were plotted using uniquely the fourth most representative data. However, in order to determine the mechanical parameters more data was used.

Those stress-strain curves concerning CNF-0% most representative samples show common tensile behavioural patterns as it may be noticed in the figure below.

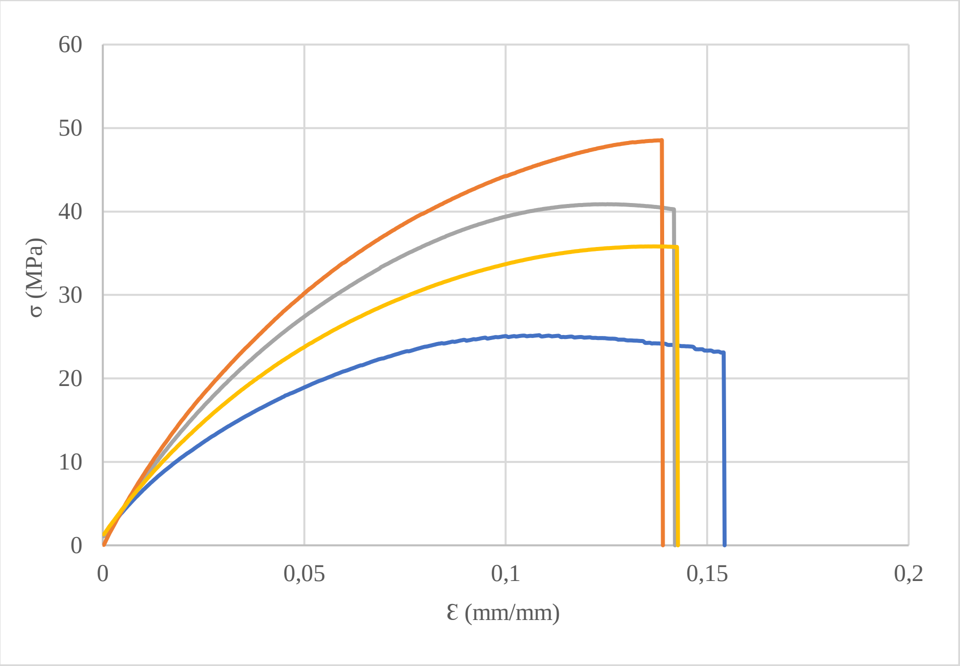

Figure 21. CNF-0% stress-strain curves of the fourth most representative samples.

Pristine PMMA films' stress-strain curves clearly exhibit a tensile pattern characteristic of a hard thermoplastic. It can also be noticed that almost all the curves broke at a strain of 15% which evince the hereinbefore mentioned brittleness of PMMA, even though the film displayed an apparent sturdiness.

It was expected that the addition of CNFs within the PMMA matrix may endow plus ductility reducing the fragility of the neat PMMA film. In return for this acquired property, those PMMA/CNFs nanocomposites will show less rigidity yet also less toughness which will lead to less ability to bear huge tensile forces. However, unawareness arises when it comes to determining at which CNF weight fraction these phenomena will be occurring.

Upon the basis of the aforementioned hypothesis, the addition of 0.5% of CNFs in the PMMA matrix slightly began to alter the mechanical properties of the films as it may be noticed in the figure below.

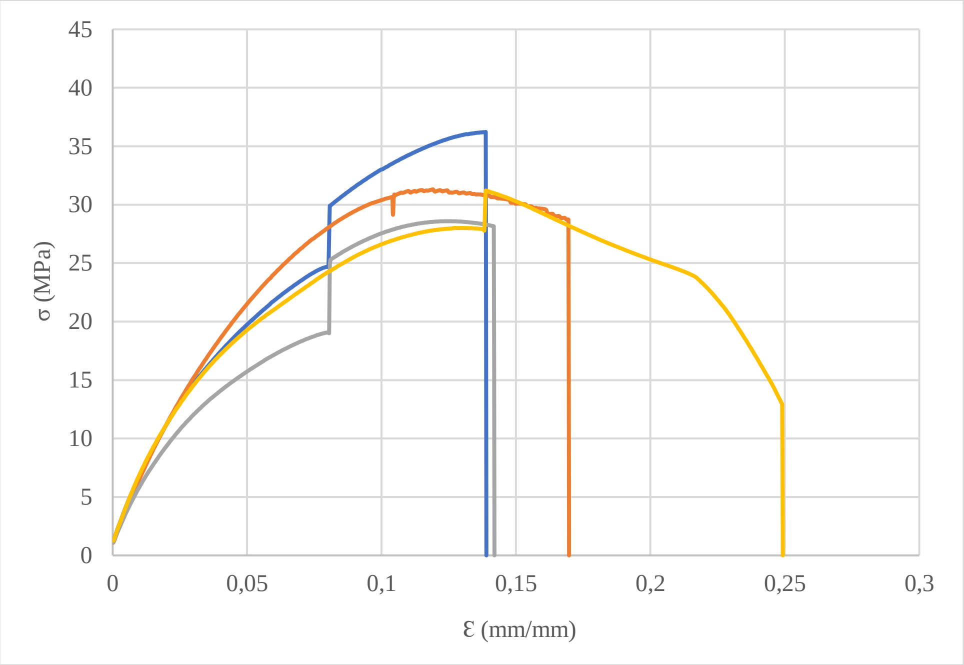

Figure 22. CNF-0.5% stress-strain curves of the fourth most representative samples.

In figure 22, it might be observed that almost all the CNF-0.5% samples broke at the same strain point than those of neat PMMA, meaning to say that ductility was not actually improved. Besides that, the curves displayed some kind of irregularities which could stem from the presence of CNFs within the matrix and the interactions that those fibres deployed all along the nanocomposite.

This tensile behavioural pattern might be due to the fact that CNF-0.5% PLM pictures definitely display no percolated framework. This sort of structure is the spatial layout needed to observe the kind of expected changes in the mechanical properties of the nanocomposite.

This CNFs entangled frame-like structure, which was sighted in CNF-1% pictures taken under the PLM, actually did change the tensile behavioural pattern of the CNF-1% stress-strain curves as it is displayed in the figure below.

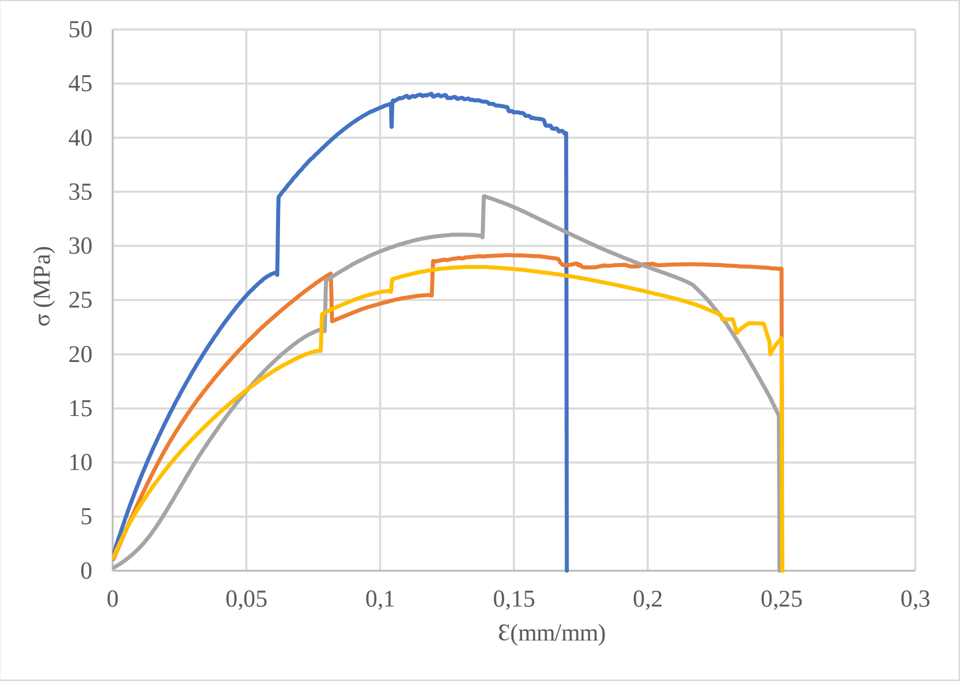

Figure 23. CNF-1% stress-strain curves of the four most representative samples.

In figure 23, it may be noticed that ultimate tensile strength of these curves is slightly lower than those of CNF-0% and that the stress-strain curves exhibit more irregularities than the previous one. However, it may also be spotted that the ductility of the material definitely had increased since most of the specimens had its breakage point occurring at 25% of strain.

The presence of the aforesaid special distribution of CNFs within the PMMA matrix of CNF-1%, which was sighted under the PLM, altogether with the increase of the ductility of the samples might be a coincidence that allow for ascertaining that the reason behind this tensile behavioural pattern might be the CNFs random and percolated framework.

In the wake of this assumption, the stress-strain curves belonging to CNF-2% test specimens exhibit a marker ductility than that of CNF-1% as it may be observed in the figure below.

In figure 24, the same kind of tensile behavioural pattern is reproduced but this in this case in a more pronounced way in terms of ductility since a couple of samples were able to elongate up to 50% of the initial gauge length. As it has been noticed in the previous graphic, the ultimate tensile strengths of CNF-2% test specimens seem to be apparently reduced by the upward content of CNFs.

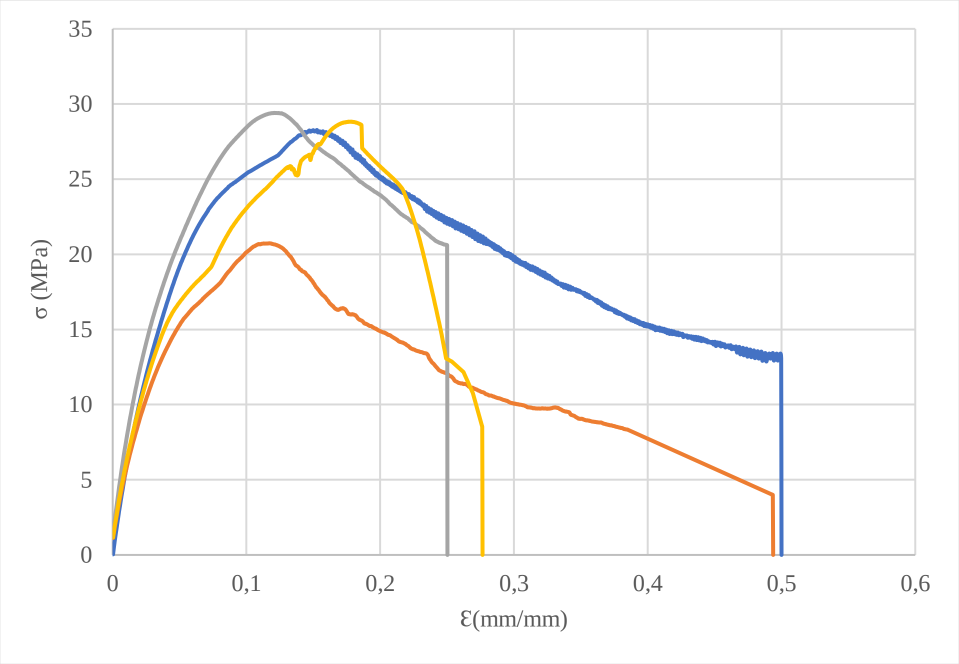

Figure 24. CNF-2% stress-strain curves of the four most representative samples.

While CNF-2% displayed a huge variation with regard the ductility of the samples, CNF-3% samples clearly elongate far more than CNF-0% as it might be observed in the figure below.

In figure 25, CNF-3% test specimen may exhibit a reduced ultimate tensile strength average in comparison with CNF-0%. Concerning the ductility, it may be noticed that 50% of elongation remain as some kind of threshold from which no type of sample neither those belonging CNF-3% nor those of CNF-2% are able to surpass without an apparent reason.

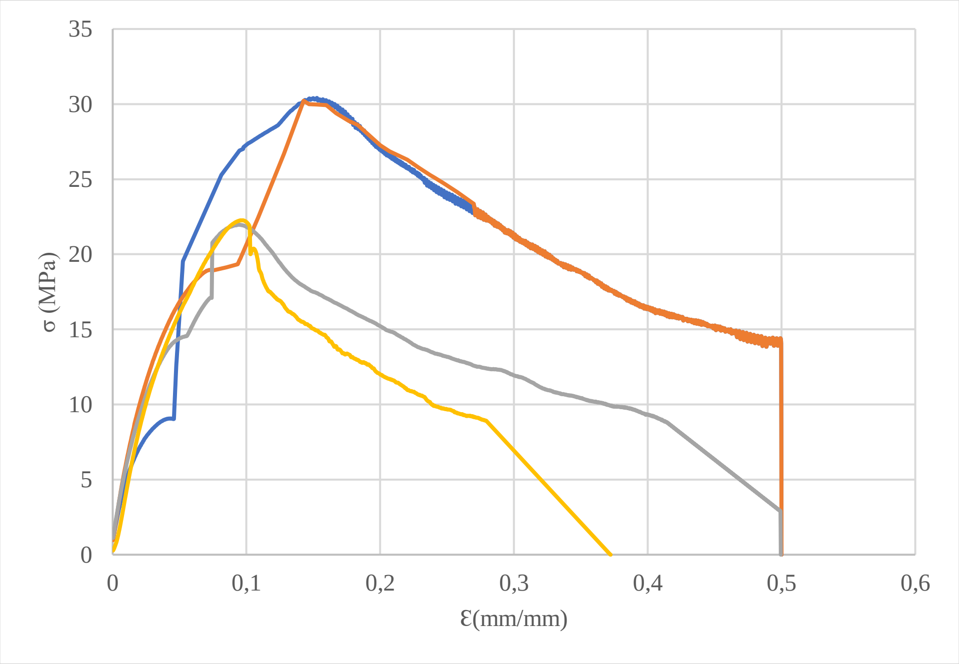

Figure 25. CNF-3% stress-strain curves of the four most representative samples.

Regarding the ultimate tensile strengths of each kind of nanocomposite, it may be deduced that as much as the CNFs content rises the lower will be the value of this mechanical magnitude. However, the variance that each sort of nanocomposite displayed in the stress-strain curve have to be considered.

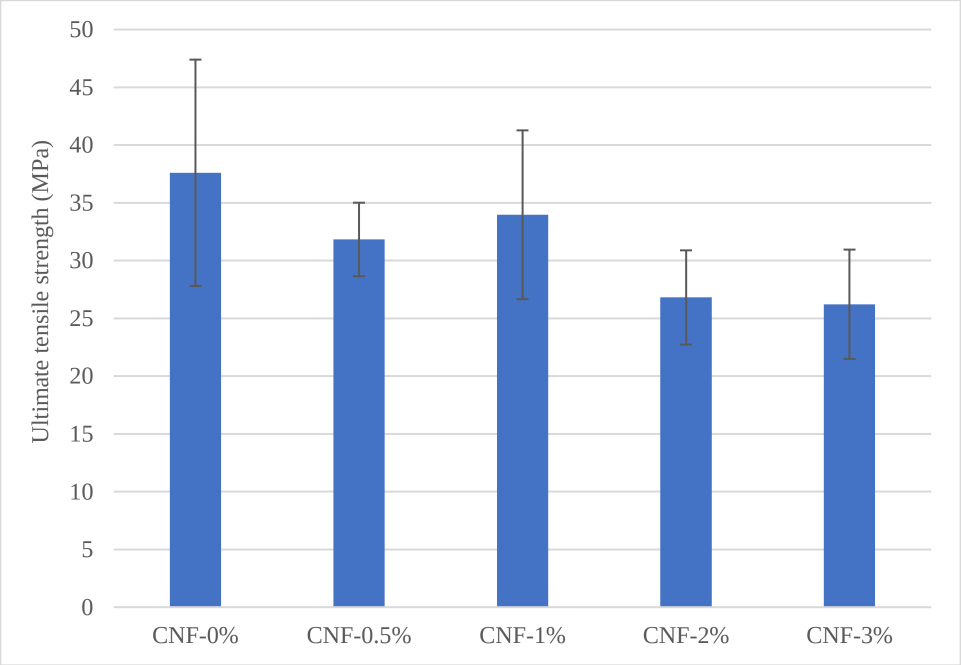

Figure 26. Ultimate tensile strength average values as regard each type of nanocomposite.

Error bars, which portray the standard deviation appearing in each type of nanocomposite with regard to the ultimate tensile strengths' values, definitely screen the variance that this magnitude shows in each kind of nanocomposite.

In figure 26, a major deviation is exhibited in CNF-0%. This fact does not allow for declaring any statistical significance upon any of the results provided for this magnitude. Despite that, it may be noticed that inasmuch as the CNF content increase, the samples display some sort of decreasing trend.

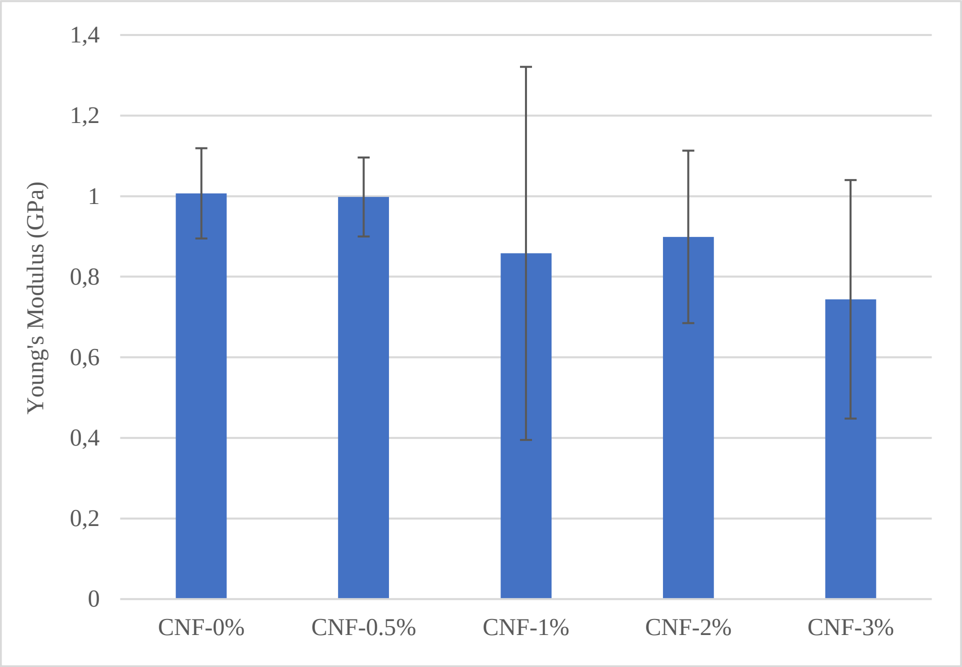

Figure 26. Young's modulus average values as regard each type of nanocomposite.

As it may be noticed in figure 27, Young’s modulus displays a similar situation than that of ultimate tensile strength. The major deviation exhibited by the samples belonging to CNF-1% clearly does not allow for any sort of statistical significance statement.

Even though, it may be noticed that this variance shows some kind of growing tendency inasmuch as the CNFs content gets higher. The origin of these remarkable variance might stem from the test specimen, the presence of CNFs or both.

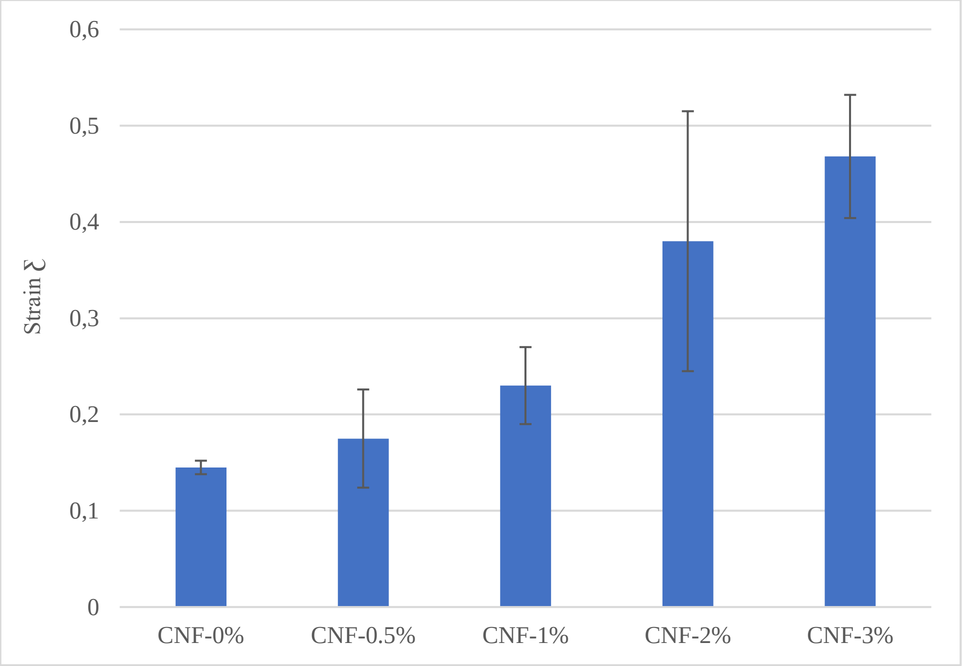

Figure 27. Strain at failure average values as regard each type of nanocomposite.

In the case of strain at failure parameter, it may be observed a statistically significant improvement upon CNF-1%, CNF-2% as well as CNF-3% with regard to CNF-0% as it is shown in figure 28. The fact that it could be stated this statistic significance is due to the minor deviation that CNF-0% samples exhibit as regard the strain at failure parameter and the fact that the samples yielded more ductility as much as the content of CNFs increased.

It may also be spotted that CNF-0,5% does not exhibit any type ductile enhancing as no random entangled CNFs framework was displayed in the PLM pictures of these samples. This comes down to say that a weight percentage higher than 0.5 wt% is needed to produce an enhancement as regard the ductility of the material.

This aforementioned weight percentage is some sort of starting point from which it could be stated that with a higher weight percentage of CNFs embedded in the PMMA matrix, a CNFs entangled network would be observed under the PLM and a statistically significant ductile enhancement would be noticed in the samples.

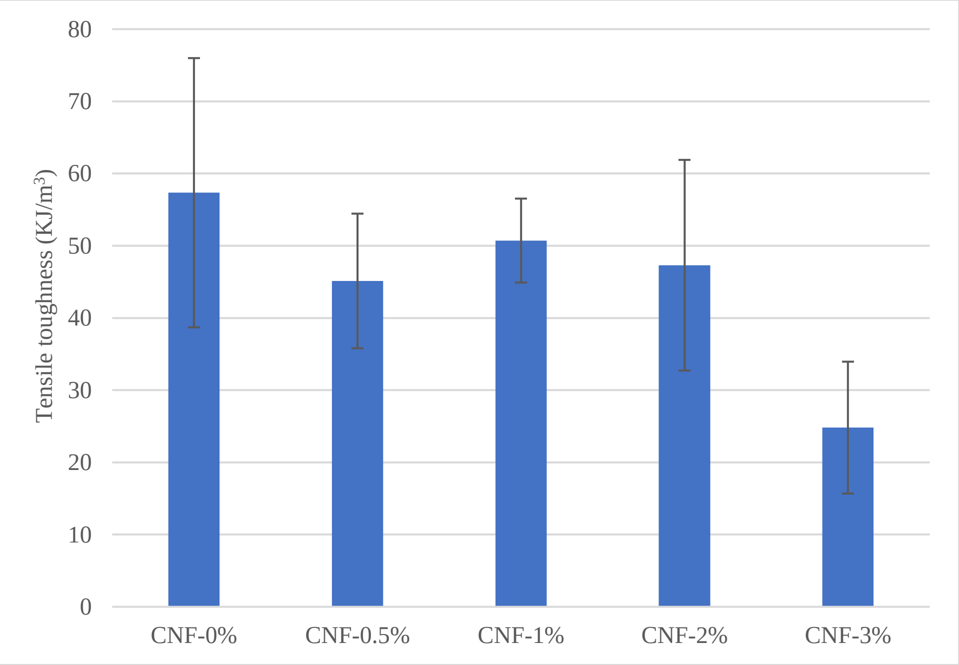

Figure 28. Tensile toughness average values as regard each type of nanocomposite.

Although it could not be noticed at first sight by just observing the previously stress-strain curves, the tensile toughness of those samples concerning CNF-3% distinctly display a statistical difference with the regard CNF-0% as it is shown in figure 29. This fact matches with the initial hypothesis, which stated that the higher the CNFs weight percentage is, the more ductile though the less tough would the material yield.

However, this reduction in toughness had only been undergone by CNF-3% samples but neither those of CNF-2% nor CNF-1% exhibit that kind of toughness diminution. Outstanding ductility displayed by CNF-3% test specimens might be the reason behind this fact noticed in figure 29. Perhaps, ductility and tensile toughness are ruled by an inversely proportional magnitude relationship.

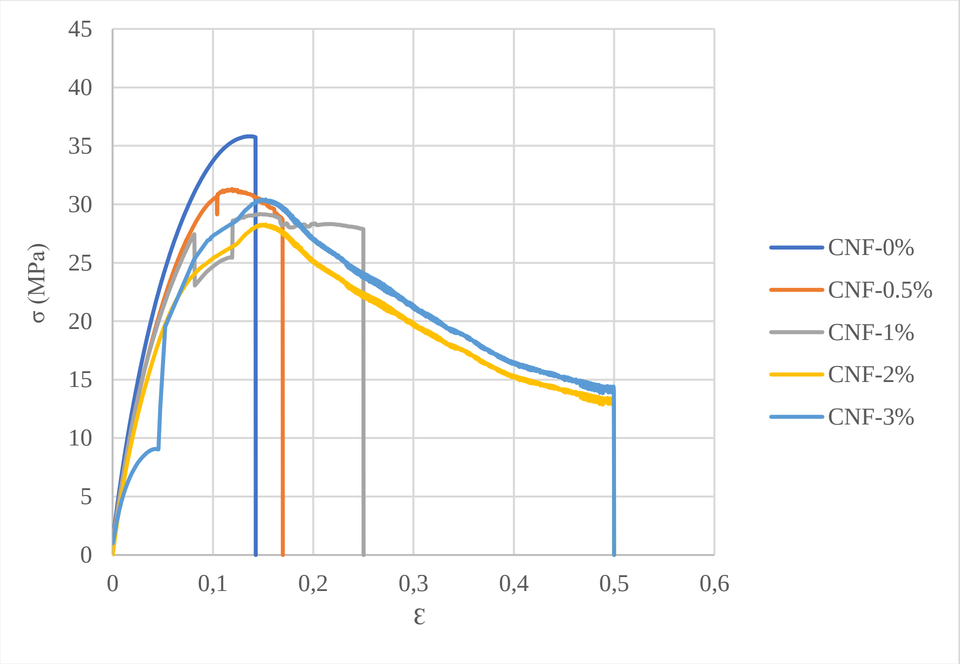

Figure 29. Stress-strain curves of every type of nanocomposite.

In figure 30, it might be observed an overlapping graphic displaying the most representative stress-strain curves of each kind of nanocomposite. As mentioned in the initial assumption, it was foreseen that with the upward addition of CNFs within the PMMA matrix the ultimate tensile strength and the Young's modulus could undergo some decreasing though this could have not been demonstrated.

However, the ductility is a mechanical parameter that has been distinctly enhanced meaning that the brittleness and rigidity of the material has been noticeably reduced as it might be spotted in the figure above. In the other hand, tensile toughness might be patchily weakened in some cases, namely CNF-3%.

5. Sustainable development

PMMA is a well-known non-biodegradable plastic whose environmental footprint does not actually accomplish with any criteria to be regarded as a sustainable material. In spite of this, PMMA long-term shelf life may make up for the fact of not being environmentally compatible and not displaying an environmentally friendly production.

However, PMMA might be recycled in many ways. As for instance, it has been proved that PMMA depolymerization obtaining highly pure MMA monomers can be achieved. (Godiya et al., 2019)Besides that, PMMA can also be re-shaped by means of the utilisation of an extruder with heat source assisting since PMMA is a thermoplastic.

Generally, pyrolysis is the only way through which PMMA can be completely disintegrated. As a result of this, recycling might be the most environmentally friendly way to handle PMMA wastes.

CNFs are made of cellulose which is known to be a natural biodegradable biopolymer. By virtue of these properties, CNFs are considered to be sustainable in an environmental point of view since this kind of cellulosic matter will be embedded within the PMMA matrix that will isolate the CNFs from the outside avoiding any kind of biodegradability. In terms of durability, we can consider that the PMMA/CNFs nanocomposite is a long-lasting material despite cellulose being biodegradable.

That means to say that from CNFs viewpoint, the PMMA/CNFs nanocomposite is considered to be environmentally sustainable as cellulose is and end-less polymer that is continuously being spawned by plants and other microorganisms.

In contrast with that, the chemicals harnessed for achieving these aforementioned CNFs might not be considered to be environmentally sustainable.

Taking the assumption that the PMMA/CNFs nanocomposite might be subjected to an extrusion process with the purpose of recycling this material. In order to take a mould of any type of pre-designed shape with any kind of PMMA already processed material, a temperature above the glass transition temperature should be needed. That prompt to state that the operational temperature on the extruder should be equal or higher than 120ºC.

All along the preparation process description, it has been mentioned that temperatures above 80-85ºC might be prone to put CNFs physical integrity in jeopardy. In the wake of this, making use of an extruder at 120ºC may be excessively risky since unawareness arise as regards the CNFs thermal degradation pattern.

This fact comes down to state that the recycling processing window of the PMMA/CNFs nanocomposite without CNFs degradation occurring is completely closed unless the policy about CNFs conservation within the recycled material change.

Within the socio-economic dimension, it has to be said that making use of PMMA in this thesis will just prompt the already wealthy and established acrylic industry. However, as hereinbefore mentioned, CNFs can be obtained from numerous sources.

Secondary cellulose reservoirs are those cellulose stocks that encompass manufactured cellulosic spin-off products from the agri-food industry. With this in mind and with the aim of choosing the most affordable and sustainable source of cellulosic materials, taking profit from these non-edible organic residues would enhance the revaluation of these wastes which could support and enhance the economy of agriculture and food industry.

In order to conclude, a suitable outlook that could aid to clarify the CNFs thermal degradation pattern to make feasible the re-utilization of the nanocomposite by means of recycling, in the best-case scenario, shall pass through performing a thermal test in order to get known if the CNFs could undergo a 120ºC recycling process without being considerably damaged.

A thermo-gravimetric analysis (TGA) and a differential-scanning calorimetry (DSC) might the most suitable thermal test that may enlighten the recycling processing issue and foster new recycling procedures to make the PMMA/CNFs more sustainable than it was before.

In spite of not be completely environmentally sustainable, PMMA/CNFs nanocomposite could play a key role within the social and the economical aspect encouraging the organic waste management industry, the food industry and also improving upon the economy of small farmers by making their wastes no longer be an expense but rather an income.

6. Conclusions

Regarding the objectives that have been set out at the beginning of this bachelor's final work it shall bespeak the following concluding statements:

- The PLM pictures of those samples concerning CNF-1%, CNF-2% as well as CNF-3% display a dispersed random distribution of CNFs assembling some sort of framework, therefore it can be stated that a scattered CNF/PMMA nanocomposite has been achieved.

- The tensile test definitely proves that CNF-1% and CNF-2% samples as well are more ductile than those of CNF-0% without other mechanical parameters being modified which means that a less brittle and equally tougher than neat PMMA PMMA/CNFs nanocomposite has been accomplished.

- Concerning Young's modulus, it can be stated that its values exhibit a powerful diminishing bias as much as the CNFs content increased, though it could not be statistically proved.

- Ultimate tensile strength, like Young's modulus, also display a decreasing trend inasmuch as the CNFs content, yet it could not be statistically signified.

- The strain at failure definitely shows a remarkable significant increase as much as the CNF content rises.

- Tensile toughness displays a progressive yet patchy weakened behaviour inasmuch as the CNF content rises. This proneness turns out to be statistically significant at CNF-3%.

- The UV-Visible transmittance measurement has demonstrated that only CNF-1% samples continue to maintain the optical clearness and transparency, thus a more ductile and equally tough yet also transparent and clear PMMA/CNFs has been accomplished.

7. Budget.

Materials and equipment cost estimation

Table 6. Table of the materials’ cost estimation.

Description	Price (€/kg)	Measures (g)	Cost (€)	Total Cost (€)
PMMA	0,77	55	0,042	50,48
CNFs	255	0,66	0,17	
DMF	141	356,5	50,27	

In table 6 is displayed the unit price of every kind of material that have been used altogether with the amounts that were mentioned in the section dealing with the preparation of the nanocomposite. The total price displayed in the same table is the material cost that will be corresponding to 10 g of each kind of nanocomposite preparation.

One of the major drawbacks that could be associated with the fact of setting up and launching an industrialized production of the CNF/PMMA nanocomposite could be the high cost production of CNFs. This cost, which stem from the functionalizing process whereby this CNFs have been isolated, cannot be reduced since the functionalization process is a key part therein precisely to make the CNFs isolation process even cheaper. The main reason behind this might be the fact that the materials needed to conduct a TEMPO-oxidation are expensive. This is some kind outlook that may need to be explored at least to reduce the production cost.

Table 7. Table of equipment’s cost estimation.

Description	Price (€/h)	Time (min)	Cost (€)	Total Cost (€)
Ultrasonicator	58	60	58	1491,33
Rotavapor	20	40	13,33	
Vacuum oven	10	5700	950	
Membrane pump	5	3600	300	
Polarized-light microscope	10	90	15	
Texturometer	30	300	150	
UV-Vis Spectrophotometer	10	30	5	

As it may be spotted in table 7, the most expensive costs concerning the preparation of the nanocomposite’s films are undoubtedly those involved in the solution/casting method hereinbefore mentioned. The vacuum, which might be considered expensive is no longer that since that vacuum allows for a higher DMF evaporation which results in less time of vacuum oven utilization and less heat power needed, which is also a huge expense. In terms of cost, is cheaper to make the void than heating the samples with the risk that might suppose to CNFs.

Total budget

The material's total cost estimation and the equipment's total cost estimation add up to 1.541,81 €, which is the total budget concerning this project.

References

Abdul Khalil, H. P. S., Davoudpour, Y., et al. (2014) 'Production and modification of nanofibrillated cellulose using various mechanical processes: A review', Carbohydrate Polymers. Elsevier Ltd., 99, pp. 649–665. doi: 10.1016/j.carbpol.2013.08.069.

Abdul Khalil, H. P. S., Davoudpour, Y, et al. (2014) 'Production and modification of nanofibrillated cellulose using various mechanical processes: A review', Carbohydrate Polymers. Elsevier Ltd., pp. 649–665. doi: 10.1016/j.carbpol.2013.08.069.

Abdulkhani, A. et al. (2015) 'a Study of Morphological, Thermal, Mechanical and Barrier Properties of Pla Based Biocomposites Prepared With Micro and Nano Sized Cellulosic Fibers', CELLULOSE CHEMISTRY AND TECHNOLOGY Cellulose Chem. Technol, 49, pp. 7–8.

Abitbol, T. et al. (2016) 'Nanocellulose, a tiny fiber with huge applications', Current Opinion in Biotechnology. Elsevier Ltd, pp. 76–88. doi: 10.1016/j.copbio.2016.01.002.

Ali, U., Karim, K. J. B. A. and Buang, N. A. (2015) 'A Review of the Properties and Applications of Poly (Methyl Methacrylate) (PMMA)', Polymer Reviews, pp. 678–705. doi: 10.1080/15583724.2015.1031377.

Altuglas, V. (2005) 'Altuglas ® v 825t', 33(June), p. 2005.

Azeredo, H. M. C., Rosa, M. F. and Mattoso, L. H. C. (2017) 'Nanocellulose in bio-based food packaging applications', Industrial Crops and Products. Elsevier B.V., 97, pp. 664–671. doi: 10.1016/j.indcrop.2016.03.013.

Campo, E. A. and Campo, E. A. (2012) 'The Complete Part Design Handbook', in The Complete Part Design Handbook. München: Carl Hanser Verlag GmbH & Co. KG, pp. I–XXI. doi: 10.3139/9783446412927. fm.

Cantor, K. M. and Watts, P. (2011) 'Plastics Materials', in Applied Plastics Engineering Handbook. Butterworths, pp. 3–5. doi: 10.1016/B978-1-4377-3514-7.10001-7.

D.Bashford, Chapman and Hall (1997) 'ACRYLICS'.

Dong, H. et al. (2015) 'Highly Transparent and Toughened Poly (methyl methacrylate) Nanocomposite Films Containing Networks of Cellulose Nanofibrils', ACS Applied Materials and Interfaces, 7(45), pp. 25464–25472. doi: 10.1021/acsami.5b08317.

Du, X. et al. (2017) 'Nanocellulose-based conductive materials and their emerging applications in energy devices - A review', Nano Energy, pp. 299–320. doi: 10.1016/j.nanoen.2017.04.001.

Ehman, N. V et al. (2016) 'From pine sawdust to cellulose nanofibres', Cellulose Chemistry and Technology, 50(3–4), pp. 361–367. Available at: https://www.scopus.com/inward/record.uri?eid=2-s2.0-84984646237&partnerID=40&md5=da41d0688a0e84e887f91cfde9ee0226.

Erbas Kiziltas, E. et al. (2015) 'Preparation and characterization of transparent PMMA-cellulose-based nanocomposites', Carbohydrate Polymers. Elsevier Ltd., 127, pp. 381–389. doi: 10.1016/j.carbpol.2015.03.029.

Ferrer, A., Pal, L. and Hubbe, M. (2017) 'Nanocellulose in packaging: Advances in barrier layer technologies', Industrial Crops and Products. Elsevier B.V., 95, pp. 574–582. doi: 10.1016/j.indcrop.2016.11.012.

Forde, N. R. (1999) 'Electronic accessibility of dissociation channels in an amide: N, N-dimethylformamide photodissociation at 193 nm', Journal of Chemical Physics, 110(18), pp. 8954–8968. doi: 10.1063/1.478898.

García, A. et al. (2016) 'Industrial and crop wastes: A new source for nanocellulose biorefinery', Industrial Crops and Products. Elsevier B.V., 93, pp. 26–38. doi: 10.1016/j.indcrop.2016.06.004.

Gibson LJ (2012) 'The heirarchial structure and mechanics of plant materials', Journal of the Royal Society Interface, 9(August), pp. 2749–2766. doi: 10.1098/rsif.2012.0341.

Godiya, C. B. et al. (2019) 'Depolymerization of waste poly (methyl methacrylate) scraps and purification of depolymerized products', Journal of Environmental Management. Elsevier, 231(August 2018), pp. 1012–1020. doi: 10.1016/j.jenvman.2018.10.116.

Gómez H., C. et al. (2016) 'Vegetable nanocellulose in food science: A review', Food Hydrocolloids, pp. 178–186. doi: 10.1016/j.foodhyd.2016.01.023.

Gooch, J. W. (2011) 'Methacrylate Ester', in Encyclopedic Dictionary of Polymers, pp. 455–455. doi: 10.1007/978-1-4419-6247-8_7373.

Halib, N. et al. (2017) 'Potential applications of nanocellulose-containing materials in the biomedical field', Materials, 10(8), pp. 1–31. doi: 10.3390/ma10080977.

Harper, C. A. and Petrie, E. M. (no date) Plastics Materials and Processes - a Concise Encyclopedia - C. Harper, E. Petrie (Wiley, 2003) WW.pdf.

Hubbe, M. A. et al. (2017) 'Nanocellulose in thin films, coatings, and plies for packaging applications: A review', BioResources, pp. 2143–2233. doi: 10.15376/biores.12.1.2143-2233.

Innventia AB, D. K. V. (2017) 'Aspects on nanofibrillated cellulose (NFC) processing, rheology and NFC-film properties', Current Opinion in Colloid & Interface Science. Elsevier Ltd, 99(1), pp. 68–75. doi: 10.1002/pc.

Isogai, A. and Bergström, L. (2018) 'Preparation of cellulose nanofibers using green and sustainable chemistry', Current Opinion in Green and Sustainable Chemistry. Elsevier B.V., 12, pp. 15–21. doi: 10.1016/j.cogsc.2018.04.008.

Isogai, A., Saito, T. and Fukuzumi, H. (2011) 'TEMPO-oxidized cellulose nanofibers', Nanoscale, pp. 71–85. doi: 10.1039/c0nr00583e.

Kalia, S. et al. (2014) 'Nanofibrillated cellulose: Surface modification and potential applications', Colloid and Polymer Science, 292(1), pp. 5–31. doi: 10.1007/s00396-013-3112-9.

Karim, Z. et al. (2016) 'Nanocellulose based functional membranes for water cleaning: Tailoring of mechanical properties, porosity and metal ion capture', Journal of Membrane Science. Elsevier, 514, pp. 418–428. doi: 10.1016/j.memsci.2016.05.018.

Lin, N. and Dufresne, A. (2014) 'Nanocellulose in biomedicine: Current status and future prospect', European Polymer Journal. Elsevier Ltd, 59, pp. 302–325. doi:

10.1016/j.eurpolymj.2014.07.025.

Mahfoudhi, N. and Boufi, S. (2017) ‘Nanocellulose as a novel nanostructured adsorbent for environmental remediation: a review’, Cellulose. Springer Netherlands, pp. 1171–1197. doi: 10.1007/s10570-017-1194-0.

Mishra, R. K., Sabu, A. and Tiwari, S. K. (2018) ‘Materials chemistry and the futurist eco-friendly applications of nanocellulose: Status and prospect’, Journal of Saudi Chemical Society. King Saud University, pp. 949–978. doi: 10.1016/j.jscs.2018.02.005.

Nechyporchuk, O. et al. (2018) ‘Production of cellulose nanofibrils: A review of recent advances’, Industrial Crops & Products. Elsevier B.V., 93(1), pp. 2–25. doi: 10.1007/s00396-013-3112-9.

Osswald, T., Baur, E., Brinkman, S., Oberbach, K., Schmachtenberg, E. (2006) International Plastics Handbook 4E - Hanser Publications. 4th edn. Hanser Publications. Available at: https://www.hanserpublications.com/Products/158-international-plastics-handbook-4e.aspx (Accessed: 7 April 2019).

Pawar, E. (2016) ‘A Review Article on Acrylic PMMA’, IOSR Journal of Mechanical and Civil Engineering (IOSR-JMCE) e-ISSN, 13(2), pp. 1–04. doi: 10.1182/blood-2006-06-029850.The.

Plappert, S. F. et al. (2018) ‘Conformal Ultrathin Coating by scCO2-Mediated PMMA Deposition: A Facile Approach to Add Moisture Resistance to Lightweight Ordered Nanocellulose Aerogels’, Chemistry of Materials, 30(7), pp. 2322–2330. doi: 10.1021/acs.chemmater.7b05226.

Rajinipriya, M. et al. (2018) ‘Importance of Agricultural and Industrial Waste in the Field of Nanocellulose and Recent Industrial Developments of Wood Based Nanocellulose: A Review’, ACS Sustainable Chemistry and Engineering, pp. 2807–2828. doi: 10.1021/acssuschemeng.7b03437.

Rodionova, G., Eriksen, Ø. and Gregersen, Ø. (2012) ‘TEMPO-oxidized cellulose nanofiber films: Effect of surface morphology on water resistance’, Cellulose, 19(4), pp. 1115–1123. doi: 10.1007/s10570-012-9721-5.

Rol, F. et al. (2019) ‘Recent advances in surface-modified cellulose nanofibrils’, Progress in Polymer Science. Elsevier Ltd, pp. 241–264. doi: 10.1016/j.progpolymsci.2018.09.002.

Saito, T. and Isogai, A. (2004) ‘TEMPO-mediated oxidation of native cellulose. The effect of oxidation conditions on chemical and crystal structures of the water-insoluble fractions’, Biomacromolecules, 5(5), pp. 1983–1989. doi: 10.1021/bm0497769.

Serra, A. et al. (2017) ‘Reducing the amount of catalyst in TEMPO-oxidized cellulose nanofibers: Effect on properties and cost’, Polymers, 9(11). doi: 10.3390/polym9110557.

Shih, Y. F. et al. (2018) ‘Highly transparent and impact-resistant PMMA nanocomposites reinforced by cellulose nanofibers of pineapple leaves modified by eco-friendly methods’, Express Polymer Letters, 12(9), pp. 844–854. doi: 10.3144/expresspolymlett.2018.72.

Thomas, B. et al. (2018) ‘Nanocellulose, a Versatile Green Platform: From Biosources to Materials and Their Applications’, Chemical Reviews, pp. 11575–11625. doi: 10.1021/acs.chemrev.7b00627.

Ummartyotin, S. et al. (2017) ‘Cellulose nanomaterials in water treatment technologies’, Industrial Crops and Products. Elsevier B.V., 59(9), pp. 5277–5287. doi: 10.1021/es506351r.

Ummartyotin, S. and Manuspiya, H. (2015) ‘A critical review on cellulose: From fundamental to an approach on sensor technology’, Renewable and Sustainable Energy Reviews. Elsevier, 41, pp. 402–412. doi: 10.1016/j.rser.2014.08.050.

Voisin, H. et al. (2017) ‘Nanocellulose-Based Materials for Water Purification’, Nanomaterials, 7(3), p. 57. doi: 10.3390/nano7030057.

Wang, X. et al. (2014) ‘Thermal, Mechanical, and Degradation Properties of Nanocomposites Prepared using Lignin-Cellulose Nanofibers and Poly(Lactic Acid)’, BioResources, 9(2), pp. 3211–3224. doi: 10.15376/biores.9.2.3211-3224.

Xu, X. et al. (2013) ‘Cellulose Nanocrystals vs. Cellulose Nanofibrils: A Comparative Study on Their Microstructures and Effects as Polymer Reinforcing Agents’, ACS applied materials & interfaces, 5, pp. 2999–3009. doi: 10.1021/am302624t.

List of figures

List of tables