



WEATHER RESISTANCE NANOCELLULOSE PAPER FOR STRUCTURAL APPLICATIONS

Lappeenranta–Lahti University of Technology LUT

Bachelor's thesis in Chemical engineering

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Examiner: Assistant professor Rama Layek

ABSTRACT

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Weather resistance nanocellulose paper for structural applications

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Sustainable development is becoming a premier concept of governments and business alike. The exhaustion of fossil reserves and impacts of global warming, eventually force us look for renewable resources to fill the demand for materials. This research aimed to study environmentally friendly biodegradable composite material made from sustainable materials cellulose nanofibrils and bark powder. Nanocellulose has a combination of outstanding properties suitable to produce strong, flexible, light, and green composite material for applications such as construction, transportation, and electronics.

Promising structural materials have been achieved by combining hydrophilic nanocellulose with hydrophobic bark powder. Mechanical study was carried out for composites. Bark powder/NFC composites proved high mechanical strength and increased elongation at break. Morphology was studied with FE-SEM, ATR-FTIR and WAXS analyses. Hydrophobicity was examined by sessile drop water contact angle. Bark powder is hydrophobic and integrating bark powder to the NFC matrix increased the hydrophobicity of the composites.

Selection of filler material for NFC matrix is important since resulting composite should have outstanding properties of hydrophobicity, mechanical strength, flexibility etc. Novel materials should have the same excellent properties as the materials they are replacing (plastics, metals, glass). Behaviour of nanocellulose itself is relatively well known and explained by its strong hydrogen bonding network. However, the network is changed when filler materials are introduced, resulting in outstanding properties.

TIIVISTELMÄ

Lappeenrannan–Lahden teknillinen yliopisto LUT

LUT Teknis-luonnontieteellinen

Kemiantekniikka

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Säänkestävä nanoselluloosapaperi rakenteellisiin sovelluksiin

Kemiantekniikan kandidaatintyö

2023

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Kestävästä kehityksestä on tulossa sekä yritysten että hallitusten johtava käsite. Ilmastonlämpenemisen vaikutukset ja fossiilisten varojen väheneminen pakottavat meidät etsimään uusiutuvia luonnonvaroja materiaalitarpeen tyydyttämiseksi. Tämän tutkimuksen tavoitteena oli tutkia ympäristöystävällistä biohajoavaa komposiittimateriaalia, joka on valmistettu kestävästä materiaaleista; nanofibrilloidusta selluloosasta ja puunkuorijauheesta. Nanoselluloosalla on erinomaisia ominaisuuksia, jotka sopivat vahvan, joustavan, kevyen ja ympäristöystävällisen komposiittimateriaalin valmistamiseen vaativiin sovelluksiin, kuten rakentamiseen, kuljetukseen ja elektroniikkaan.

Lupaava rakennemateriaali saatiin yhdistämällä hydrofiilistä nanoselluloosaa hydrofobiseen puunkuorijauheeseen. Komposiiteille tehtiin mekaanisia tutkimuksia. Komposiiteilla oli korkea mekaaninen lujuus ja murtovenymä. Morfologiaa tutkittiin FE-SEM-, ATR-FTIR- ja WAXS-analyyseillä. Hydrofobisuutta tutkittiin veden kontaktikulmamittausten avulla. Puunkuorijauhe on hydrofobista, joten kuorijauheen lisääminen NFC-matriisiin lisäsi komposiittien hydrofobisuutta.

Täyteaineen valinta NFC-matriisiin on tärkeää, sillä tuloksena syntyvällä komposiitilla tulee olla mm. erinomainen hydrofobisuus, mekaaninen lujuus ja joustavuus. Uusilla materiaaleilla tulee olla samat hyvät ominaisuudet kuin materiaaleilla, joita ne korvaavat (muovit, metallit, lasi). Nanoselluloosan ominaisuudet tunnetaan suhteellisen hyvin ja ne selittyvät sen vahvalla vetysidosverkostolla. Sidokset muuttuvat, kun selluloosaa muokataan lisäämällä siihen täyteaineita. Täten saadaan uusia ominaisuuksia.

SYMBOLS AND ABBREVIATIONS

Roman characters

d	lattice spacing	[nm]
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Greek characters

θ	Braggs angle	[°]
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λ	X-ray wavelength	[nm]
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Constants

λ	Copper pipe wavelength	0.154 nm
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Abbreviations

CNF	Cellulose nanofibrils
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NFC	Nanofibrillated cellulose
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Water	Deionized water
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Wt%	Weight percentage
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1 Introduction

Background of the topic and importance of it are discussed in this introductory chapter. Research problem, objectives and research questions are set. Finally, the methods to investigate the research problem and answer to the research questions are explained.

1.1 Background

Petroleum based products have long known to be unsustainable and harmful to the environment as they are derived from fossil fuel-based resources and are not degrading after use (Barnes et al., 2009; Sethi et al., 2021). However, many demanding applications such as construction, structural composites, flexible packaging, and electronic applications need strong, ductile, and elastic materials with enhanced environmental sustainability. Among various types of applications structural composites are attractive due to their light weight and outstanding properties. (Farooq et al., 2018; Shekar & Ramachandra, 2018; Symington et al., 2009) Petroleum based plastic and their composites with carbon fiber and glass fiber for example have desired properties and they are lightweight as well (Barnes et al., 2009).

With current rate of consuming virgin raw materials like petroleum and glass in building, sustainability is not achieved. The majority of fossil-based composite and polymer material is not degrading to the environment. (Barnes et al., 2009) Also, the petroleum sources are alarmingly decreasing (Barnes et al., 2009; Henriksson et al., 2008). Innovative solutions are needed. The structural components of structural composites must have outstanding sustainability and ability to perform well in moist environments. (Sethi, Farooq, Österberg, et al., 2018) This thesis will focus on ductility and hydrophobicity of biobased sustainable biopolymer composite.

Among various types of sustainable biobased materials, nanofibrillated cellulose (NFC) has outstanding paper like film forming ability. On the surface of the NFC, there are several oxygen-containing functional groups that can bond the cellulose nanofibrils together via hydrogen-bonding interaction and brings high mechanical properties. (Abitbol et al., 2016;

Trache et al., 2017) Additionally, it exhibits outstanding environmental greenness, abundant feedstock, renewable resources, high aspect ratio, light weight, remarkable strength, and stiffness. That makes the nanocellulose an attractive biopolymeric material for sustainable products and solutions like application in various demanding areas including structural composites. (Abitbol et al., 2016; K. Y. Lee et al., 2014; Mautner et al., 2020; Trache et al., 2017) Nanocellulose has many sources, and it is available widely (Abitbol et al., 2016). It can be extracted from trees for example (Trache et al., 2017; Wang et al., 2022). Also fibrillated nanocellulose could be isolated from side streams of industrial side streams, for example birch sawdust, ever-dried dissolving cellulose and non-dried dissolving cellulose residues (Jonoobi et al., 2012; Liu et al., 2014). However, nanocellulose paper is hydrophilic in nature which causes deterioration of mechanical properties in humid environments (K. Y. Lee et al., 2014).

Nanofibrillated cellulose (NFC) also referred as cellulose nanofibrils (CNF) refers to cellulose fibers that form nanofibril units; fibrils are nanoscale (less than 100 nm) in diameter and typically several micrometers long (Abitbol et al., 2016). Nanocellulose paper has been studied to see if it could form a water-repellent, durable, and flexible component to be used with another compound to form composite for structural composite applications (Abitbol et al., 2016; K. Y. Lee et al., 2014; Trache et al., 2017). In this research bark powder is combined with NFC. Large amount of bark is available from wood processing industry side streams (Pásztor et al., 2016). Bark is a sustainable material that could be used in many applications but is currently considered as waste and mainly used for energy production (Holmbom, 2019).

1.2 Research problem and objectives

The problem is that nanocellulose paper is hydrophilic in nature and deteriorates in humid environments (K. Y. Lee et al., 2014). The structural components of structural composites must have outstanding sustainability and ability to perform well in moist environments. Fossil-based products must be gradually replaced (Henriksson et al., 2008; Sethi et al., 2021) but it is not simple to find substituting materials with these outstanding properties.

The goal of this thesis is to fabricate hydrophobic nanocellulose paper with enhanced water resistance property. Bark powder is used to modify NFC for making cellulose nanofibrils more hydrophobic and applicable in composite materials. Product could be used as an alternative material for structural components instead of petroleum-based products. In some structural applications modified nanocellulose paper composite could also replace metal-, laminate-, and ceramic composites. (Abitbol et al., 2016)

In this thesis, answers to the following questions are searched. Does bark powder integration to NFC make the material hydrophobic? How do tensile properties of NFC film change if bark powder is blended in different concentrations? Could nanocellulose-bark powder composite replace oil-based plastics? How the chemistry of compatibilization works between hydrophilic NFC and hydrophobic bark powder? What causes the change in hydrophobicity and ductility? What other compounds could be added to nanocellulose instead of bark powder?

Nanocellulose paper has been studied to be strong and easily biodegradable (Abitbol et al., 2016; Trache et al., 2017). However, it is also known that the material is hydrophilic and deteriorates performance in moist condition. This thesis will focus on addressing these unwanted properties. Laboratory work is performed trying to combine the functionality of bark powder and nanocellulose in a single bark powder/NFC composite paper via tailoring the interfacial interaction chemistry between bark and NFC to improve water resistance property and ductility of the NFC paper.

1.3 Importance

The surface of NFC paper must be modified to achieve the desired properties (Abdul Khalil et al., 2014; Hoo et al., 2022; Lv et al., 2023). Nature offers many examples of water repellent materials; fish skin, eucalyptus leaves and trunk does not let water in or out unless damaged (Franco et al., n.d.; Rakhmatullina et al., 2022). That raises interest towards hydrophobic bark powder which is the material that covers trunks in the outer surface. It is highly hydrophobic to protect the tree. (Korpinen et al., 2022) Adding bark powder to NFC could give it the desired properties of hydrophobicity and mechanical strength. This research is

important, because previously no research has been undertaken on the use of bark powder in the production of nanofibrillated cellulose paper. Neither has its effect on the product's hydrophobicity and durability been studied.

The results of the research can be used in the green transition to a fossil-free future. If the properties of the nanocellulose-bark composite paper turn out to be desirable, production on a larger scale could be possible after economical cost-benefit analysis has been executed. Innovative solutions facilitate the transition away from non-environmentally friendly materials to greener solutions. It is reported that both individual component of NFC and bark powder are biodegradable (Alonso et al., 2017; Korpinen et al., 2022) and hence, our NFC-bark composite paper should be completely biodegradable and a green choice. No chemicals have been used in its manufacturing. The material can be used in structural applications, and perhaps also in food packaging.

1.4 Methods

This Bachelor's thesis will include literature review and experimental work. Experimental work includes preparation of the nanocellulose paper from fibrillated nanocellulose dispersion and bark powder in different concentrations. One is reference sample, pure NFC film. The intention is to modify the -OH bonds of nanocellulose. Tensile strength and contact angle of the material are tested to get information about mechanical properties and hydrophobicity. Information about morphology and bonding is acquired with FE-SEM, WAXS and ATR-FTIR analyses.

Literature work includes reviewing research about the topic. Trying to find answers to the following questions: What is the source of nanofibrillated cellulose? What material has other researchers introduced on hydrophilic nanocellulose paper; what are other possibilities to increase nanocellulose paper mechanical properties? Literature on nanocomposites and suitability of nanofibrillated cellulose as reinforcement in composite is studied.

2 Literature review

In this chapter the structure of cellulose is explained. Sources of cellulose and the methods for breaking cellulose into nanosized fibrils are discussed. Definition of composites and specifically nanocomposites is given. Explanation about the outstanding opportunity of using NFC as reinforcement in composites is described to justify the choice for studying nanofibrillated cellulose as a material for environmentally friendly alternative for plastics.

2.1 Source of NFC

The primary source of cellulose is the lignocellulosic material, especially wood in forests. Cellulose also occurs in agriculture residues, water plants etc. material derived from plants. These substances also contain hemicellulose and lignin. (Abdul Khalil et al., 2012) Cellulose as raw material is considered nearly inexhaustible (Klemm et al., 2005).

Cellulose is a carbohydrate polymer that consists of repeating units of β -D-glucopyranose. Repeating units are joined by glycosidic linkages. (Abdul Khalil et al., 2012) Two glucopyranose units linked with a glycosidic linkage is shown in figure 1.

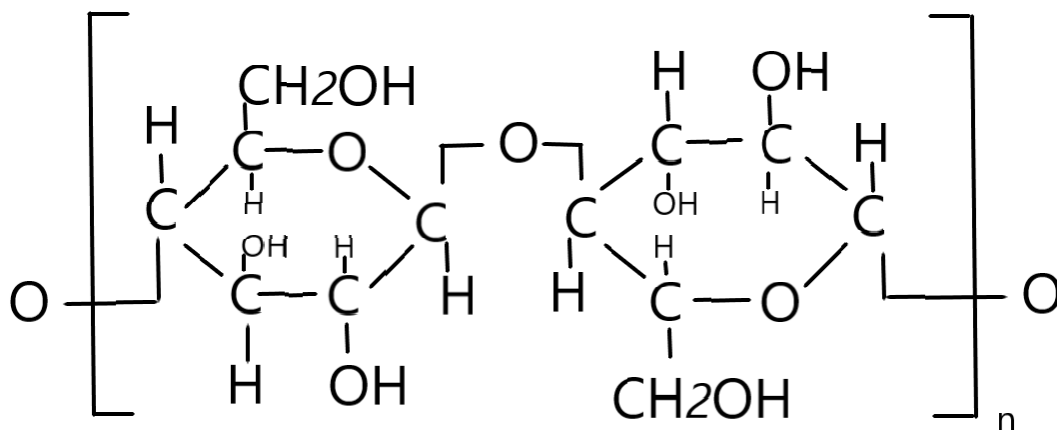


Figure 1. Repeating units of cellulose. β -D-glucopyranose linked with a glycosidic linkage.

Cellulose fibers have unique structural hierarchy as they consist of nanofiber assemblies that have a diameter from 2 to 20 nanometers with length of a few micrometers. There are several sources of these nanometer-sized fibers of cellulose, some to mention: wood, cotton, pineapple leaf and sisal. (Abdul Khalil et al., 2012)

Nanocellulose fibers are interesting because they are highly crystalline and most importantly are in abundance in plant bodies. They also differ from the synthetically manufactured nanofibers. Cellulose nanofibers can form extremely strong and transparent films that can be exploited in many areas. In plant cell walls there are numerous hydrogen bonds between cellulose microfibrils. These bonds bind the units tightly together. Converting native cellulose into individual nanofibrils is impossible without reducing the structural potential of the length of nanofibrils. (Abdul Khalil et al., 2012)

Many processes to disintegrate cellulosic material into nanocellulose have been reported (Eichhorn et al., 2010). Mechanical methods (cryocrushing) (Chakraborty et al., 2005), chemical methods (acid hydrolysis) (Elazzouzi-Hafraoui et al., 2008), high pressure homogenization (Nakagaito & Yano, 2004) and ultrasonic techniques (Cheng et al., 2010) to name a few. The resulting nanofibrillar material differs depending on the disintegration process. Also, pretreatment and source of raw material affect the result. Process usually starts with mechanical or chemical pulping where liberation of fibers from the wood matrix takes place. (Abdul Khalil et al., 2012) Mechanical pulping is more energy consuming and leads to generation of fines which are below nanoscale particles. However, in mechanical pulping wood material is efficiently used while in chemical pulping half of the wood material is dissolved. (Gellerstedt et al., 2009)

Challenge in the preparation of nanofibrils is high energy consumption. To yield good defibrillation and high-quality fibrils many cycles of fibrillation is needed. (Zhang et al., 2012) With suitable combination of mechanical, biological, enzymatic, and chemical pretreatments the size of fibers can be reduced before fibrillation. Less mechanical work is needed to get into nanoscale fibrils and therefore less energy is needed. (Abdul Khalil et al., 2014)

Nanocellulose fibers can be produced with micronization techniques; high-pressure homogenization, microfluidization or high-speed friction grinding. These processes reduce the diameter of solid particles. Although these mechanical methods are efficient for producing the high quality nanofibrillated material, pretreatment strategies are needed to facilitate the fibrillation of cellulose fibers and decrease the energy consumption. (Levanič et al., 2020)

Lack of pretreatment is not desirable, however excessive pretreatment can also be a trouble. Potential problems of excessive pretreatment are excessive disintegration of fibers and generation of fines. These are not desirable outcomes in the subsequent process stages. For optimizing the benefits of pretreatment and control the generation of fines morphological analysis and fine content analysis can be conducted. (Levanič et al., 2020)

2.2 Composites

Composite is a fusion of two materials that are different in their physical or chemical properties; usually a reinforcement and a matrix (Ashutosh et al., 2016). These two materials form a functional entity without mixing with each other. Unique properties from different materials combine and form synergistic effects. (Ashutosh et al., 2016; Vuorinen et al., 2016) Examples on use of composites are sports equipment and wind turbine blades. An increasing number of composites are also used in the boat industry and construction materials. In modern airplanes, more than half of the structures are already composites. (Vuorinen et al., 2016)

The matrix works as a glue that binds the reinforcements together and protects them from the environment. Reinforcements is a general name for fibers/particles inside the matrix. (Doughett & Asnarez, 2010; Vuorinen et al., 2016) In addition to strength, reinforcements can change stiffness, electrical conductivity, and thermal conductivity. As a matrix of composites plastic can be used (plastic composites, polymer composites). Also, ceramic can be a matrix (ceramic matrix composites) and metal (metal matrix composites). Plastics are commonly used in composites due to their lightweight. In the future, biopolymers will be increasingly used as matrices. (Ashutosh et al., 2016; Vuorinen et al., 2016) Biopolymers

refer to bio-based plastics, an example is lactic acid-based polylactide or PLA (Vuorinen et al., 2016).

Fiberglass is currently the most used reinforcing fiber. Fiberglass has great strength, and its rigidity is of the same magnitude as aluminium's. Fiberglass is also more affordable than other reinforcing fibers. Individual glass fiber has typically diameter of 17 μm . Natural fibers are an interesting new class of reinforcements, and they are divided into three different groups: plant fibers, mineral fibers and animal fibers. Plant fibers are formed mainly from cellulose. (Vuorinen et al., 2016) The properties of fiber-reinforced composites depend on the type, length, quantity, and direction of the fiber (Symington et al., 2009; Vuorinen et al., 2016). The best mechanical properties relative to weight are obtained when all the fibers are parallel (Vuorinen et al., 2016).

2.2.1 Nanocomposites

Nanocomposites are two-phase materials, and the other phase must have at least one nanometer range (1-100 nm) dimension (diameter, length etc.) Nanocomposites dominate conventional composites with their mechanical and thermal properties, transparency, better recyclability, and low weight. (Oksman et al., 2006; Sorrentino et al., 2007) Biopolymer-based nanocomposites have been researched recently a lot (Abdul Khalil et al., 2012; Sorrentino et al., 2007).

In nanocomposite processes, the nanoparticles are compiled with other materials like polymers, metals, or nanoparticles. The goal is to formulate the assembly so that there is maximal interactivity between the materials. Final size and properties of composite are influenced by the interaction between matrix and reinforcement. (Shalan et al., 2021)

The research field on nanocomposites is ever-growing. Many nanoscale composites have gained space on markets. Uses of nanocomposites include automotive panels, solar cells, furniture, bulletin boards and bone cement for example. There is demand for nanocomposites from various areas like wastewater treatment applications, building, and biomedicine where precise dimensions are essential to solve application difficulties. (Abitbol et al., 2016; Shalan

et al., 2021) Nanocomposites' excellent features are supported by their large number of functional groups, pore-forming characteristics, easy recovery, and enhanced monitoring potential and treatment procedure (Abitbol et al., 2016; Wang et al., 2022).

As nanomaterials have outstanding properties, they are often mixed with bulk polymeric material. Together they have better properties than bulk alone. Depending on the matrix material, division is made into polymer matrix composites, ceramic matrix composites and metal matrix composites. (Shalan et al., 2021; Vuorinen et al., 2016) When combining nanomaterial and polymer matrix it is essential to consider proper dispersion of the nanofillers in the bulk material. Only homogenous distribution of nanofiller enhances the properties of polymer matrix. However, the dispersion is not straightforward - nanomaterial have tendency to particle agglomeration caused by the van der Waals forces. That deteriorates properties. (Shalan et al., 2021)

Functionalization and surface modification of nanomaterials have been studied to increase the interfacial interaction (compatibility) between the nanofiller and matrix (Eichhorn et al., 2010). As a result, better dispersion is achieved and that facilitates effective stress transfer from filler to matrix developing lightweight high-performance composites for demanding applications. (Shalan et al., 2021)

2.2.2 Structural applications

Structural applications include construction (e.g., building and roads), and vehicle manufacturing (automotive, aerospace), energy production (turbine blades), body protection (helmets and body armor). In structural applications materials primary purpose is to transfer or support a force. (Pero-Sanz Elorz et al., 2019)

Structural materials are materials subjected to loads in their service. Loads generate tension stresses, bending and compression stresses, fatigue, etc. These mechanical properties ("bulk properties") must sometimes be reinforced with other properties like resistance to oxidation and corrosion, antifriction behaviour etc. The tensile test is the most used proof to measure

the mechanical properties of the structural material. Stiffness, elasticity, mechanical resistance, toughness are useful properties in construction. (Pero-Sanz Elorz et al., 2019)

Laminates and sandwich panels are subclass of structural composites (Paul & Dai, 2018). Laminate is used in floor materials and sandwich panels in aerospace, civil engineering, and other industries for example (Rejab & Cantwell, 2013). Building materials and laminates require high mechanical properties and load bearing (Gribniak, 2021). In outdoor structural applications moisture absorption resistance is essential. The outdoor environment is challenging and versatile. Therefore composites made from biodegradable polymers and novel nanomaterials may require improvement in low thermal stability, brittleness, and poor barrier properties (Sorrentino et al., 2007).

Structural applications must have long-lasting material that does not lose its properties during the lifetime. With correct planning and choice of material, fully bio-derived nanocomposites can be used, and the fossil materials can eventually be replaced. (Oksman et al., 2006)

Construction industry is using huge amounts of concrete, metal, plastics, and glass (Barnes et al., 2009). Construction industry is therefore responsible for environmental impact and use of vast amounts of materials. If adequate characterization and optimization is done for new materials environmentally friendly efficient lower cost materials can be implemented to construction guaranteeing the required structural safety simultaneously. (Gribniak, 2021)

Fiber-reinforced polymer materials have been researched to strengthen concrete structures. Publications revealed that the application of nanoparticles can enhance the mechanical performance of structural composite materials. Some of the issues encountered in structural applications field are resonance problems, sound radiation/vibration of composites, safety, temperature changes and cracking behaviour. (Gribniak, 2021) Nanoparticles has been reported to improve the mechanical performance of composite materials (Kumar et al., 2020). The structural advances of fiber-reinforced matrices are affected by the content and the mechanical and geometrical properties of the fiber. Toughness can be increased significantly, and ductility is promoted. (Gribniak, 2021)

2.3 NFC paper

The cellulose crystals have high stiffness and can therefore be used for composite materials as reinforcement. High stiffness can be exploited by disintegrating plant (source of cellulose) into fibrous individual nanofibers (also called nanowhiskers) which reduces the amount of amorphous matter in the material. Nanofibrils are suitable for reinforcement since they have high aspect ratio (length/diameter). High aspect ratio is desirable in composite materials as stress can be transferred through length from matrix material to reinforcing phase. (Abdul Khalil et al., 2012; Abitbol et al., 2016)

Using NFC in composites is not completely new case (Eichhorn et al., 2010). First NFC containing nanocomposites were prepared already in 1983. Nanofibrils were made by hydrolysing softwood pulp with hydrochloric acid (HCl) and suspension was pumped through slit homogenizer. NFC was used as reinforcing filler for thermoplastics. (Boldizar et al., 1987) The research on cellulosic nanofibres as reinforcing phase in nanocomposites started approximately 15 years ago. Enormous amount of literature has been written since and the topic is still gaining a lot of attention (Eichhorn et al., 2010; Shekar & Ramachandra, 2018).

Nanofibrillated cellulose paper has layer-by-layer structure. Therefore, fibrils can remarkably interact with each other and the surrounding matrix. That can significantly enhance the mechanical properties of the resulting material. Cellulose nanofibrils have a high surface area to volume ratio. In other words, the fibrils' surface has a dominant role in mechanical efficiency of stress transfer. High surface area also creates possibility to chemically modify the surface. (Abdul Khalil et al., 2012; K. Y. Lee et al., 2014)

Evidence has been found that there is relationship between hydrogen bonding interactions and enhancement of properties of nanocellulose based bionanocomposites (Nishiyama, 2018; Shekar & Ramachandra, 2018). New hydrogen bonds form when composite materials are combined and that is the main factor contributing to composites' final properties (Abdul Khalil et al., 2012; Doughett & Asnarez, 2010).

Cellulose has network of hydrogen bonds which makes it comparably stable polymer. Cellulose does not have melting point. Due to the hydrogen bond network cellulose chains

possess high axial stiffness. High stiffness as mechanical property is desirable for a reinforcing fibre in a composite. (Eichhorn et al., 2010)

Nanocellulose is generally modified to improve compatibility with non-polar polymers. Nanocellulose paper is strongly polar due to many -OH groups in its structure. Modification also has reported to decrease surface energy, increase surface roughness, and thus enhance hydrophobicity. (Abdul Khalil et al., 2012) However, it must be considered that these surface modifications can reduce the interactions among the nanofibrils and as consequence change the mechanical properties of the corresponding nanocomposites in macroscopic level.

Fibrillated nanocellulose paper is ideal reinforcement for polymer matrix. Cellulose nanofibers have researched to increase the Young's modulus (ratio of tensile stress per strain) and tensile strength of composites due to the strong interactions between starch matrix and the high aspect ratio nanofibers. (K. Y. Lee et al., 2014)

2.4 Approaches to modify NFC

Nanocellulose has several surface hydroxyl groups and relatively large specific surface area. Therefore, it provides active sites for modifying nanocellulose surface. Covalent modifications e.g., oxidation (Sun et al., 2015), polymer grafting (Hemraz et al., 2015) and noncovalent binding (Villares et al., 2015) are proposed methods to integrate functional groups on nanocellulose surfaces and also as precursors for further modification. (Abitbol et al., 2016)

Bark, which is studied in this research in combination with NFC is a sustainable source of biopolymer (Korpinen et al., 2022). Huge amounts of bark is released from the wood processing industry as a side stream. Most of it is unfortunately used for energy instead of utilized as potential green chemicals. (Gandini et al., 2006; Holmbom, 2019) It is estimated that globally 300-400 million m³ of bark is generated per year (Pásztor et al., 2016).

There exist several other hydrophobic synthetic and natural materials. Therefore, it is evitable that bark powder is not the only material that could be used as reinforcement with

NFC composite. There are numerous studies for making cellulose nanofibrils more hydrophobic and applicable in composite materials. Epoxy (Ansari et al., 2014; Nissilä et al., 2019), reduced graphene oxide (Duan et al., 2016; Volfkovich et al., 2022), polyurethane (Sethi, Farooq, Österberg, et al., 2018) and lactic acid (Sethi et al., 2021) modified cellulose nanopapers are for example studied.

2.4.1 Epoxy

Nissilä et al. have studied a method for preparing epoxy-cellulose nanofiber composite paper with an oriented structure. They used ice-templating (or freeze-casting) to produce porous CNF networks with pores with a diameter from ten to hundreds of micrometers.

Bio-epoxy (with 21% biobased carbon content) resin was the polymer matrix in the cellulose nanocomposites. CNFs were received from bleached softwood pulp through mechanical fibrillation. Suspension was filtrated through an ultrafine grinder. The resulting CNF suspension consisted mostly of nanofibers. The process resulted in a transparent and thin sheet of nanocomposite material. Flexural and tensile experiments of the composite and epoxy samples were carried out. (Nissilä et al., 2019)

Cellulose nanocomposites were measured with higher elastic moduli than that of neat epoxy. The stiffness of the material is increased by network-like CNF reinforcement phase inside the matrix. Mechanical properties had improved less than expected. It could be explained by the “fact that the impregnation does not seem to have occurred at the single fiber level”. (Nissilä et al., 2019) Lee et al. has presented the explanation to apply for most of the CNF networks with resin-impregnation (K. Y. Lee et al., 2014).

2.4.2 Graphene

Graphene has outstanding mechanical, and physical properties. (Layek & Nandi, 2013) Due to promising mechanical and electrical properties, NFC composites with graphene modification are finding significant interest for numerous demanding applications (structural films, flexible electronic device packaging films, and other hybrid materials). (Duan et al.,

2016) Graphene oxide (GO)/NFC composite papers address improved mechanical properties. The interfacial interaction between the hydrophilic oxygen containing functional groups of GO and NFC create outstanding properties. However, oxygen-containing functional groups that are hydrophilic, easily absorb moisture from the environment, and therefore reduce the performance of graphene/NFC composite films. Majority of the graphene/nanocellulose composite nanopapers are either hydrophilic, or less ductile (stiff and brittle composite). (Layek et al., 2021)

Layek et al. show that the challenges of graphene/NFC composites may be defeated by generating additional functionalities such as ductility, toughness, and hydrophobicity in graphene/NFC composite films “via tailoring the chemical functionalities and interfacial interaction between NFC and graphene or derivatives of graphene” (Layek et al., 2021).

Layek et al. reported the synthesis of a novel NFC-graft-PIL (polyionic liquid) containing hydrophobic pyridyl hexyl chains and its freestanding composite paper with hydrophobic rGO (reduced graphene oxide). rGO/NFC-g-PIL paper showed higher hydrophobicity and ductility with respect to NFC paper. Significant enhancement of mechanical strength was also reported. (Layek et al., 2021)

2.4.3 Polyurethane

Sethi et al. attempted to improve the wet mechanical properties of cellulose nanopaper by integrating polyurethane (PU). Water based PU was diffused along with CNFs to form hybrid nanopapers. (Sethi, Farooq, Österberg, et al., 2018)

The nanopapers were water resistant on other surface (PU modified side) while hydrophilic on the cellulose rich side, so the paper was stereoselectively water resistant. The hybrid nanopapers had higher elongation, tensile strength and enhanced thermal stability. The material has relevant properties to be used in flexible electronics and transparent displays. (Sethi, Farooq, Österberg, et al., 2018)

2.4.4 Lactic acid

Sethi et al. have reported in three research papers that sonication-assisted lactic acid (LA) modification drastically shortens the draining time by reducing water retention in nanopapers (Sethi et al., 2021; Sethi, Farooq, Sain, et al., 2018; Sethi, Oksman, et al., 2018). They used LA modification of CNFs in combination with centrifugation. They succeeded to get rid of water without vacuum filtration resulting in significantly shorter preparation time. Nanopapers were dry and ready to use in 15 min with LA modification. (Sethi et al., 2021)

The nanopapers were characterized by their mechanical properties and morphology. The researchers reported that mixture of LA-modified CNFs could be shaped into a thin film by simply pressing. If dried in a vacuum solid nanopaper could be obtained.

The water retention value (water holding capacity) of the CNF decreased from 66 to 26% for LA-modified CNFs compared to pure CNFs indicating more hydrophobicity. Mechanical characteristics were compared to values reported in the literature. Nanopapers obtained from the centrifugal drying instead of vacuum filtration and other draining methods were similar or better. The reference (unmodified CNFs) had similar tensile modulus, but the tensile strength decreased in LA-modified nanopapers by 30%. They supposed that was “because of the presence of LA moieties at the interface, which likely reduced the hydrogen bonding between the CNFs (Benítez et al., 2013)”. (Sethi et al., 2021)

3 Experimental section

In this chapter materials and experimental procedures are presented. Preparation of samples and the analysis methods and their importance are discussed. Figure 2 is a simplified schematic representation about the whole process.

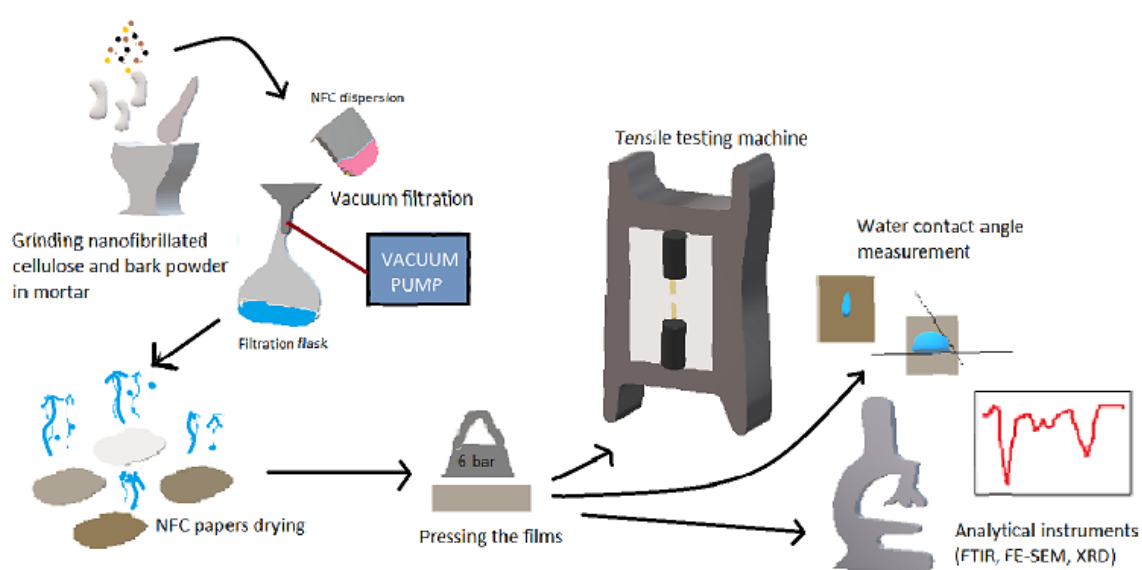


Figure 2. Schematic representation of the experimental process and methods.

In the beginning nanofibrillated cellulose and bark powder was grinded, and dispersion was prepared. Dispersion was vacuum filtered and dried. After that it was pressed and prepared for further analysing. Each stage is explained in detail in the following chapters.

3.1 Materials

Cellulose nanofibrils are from the University of Maine. CNF is in cake form with solid content 15 wt% in water. Grade is 90 % fines. Raw material is shown in figure 3. CNF is the matrix in the bark powder/NFC composite.

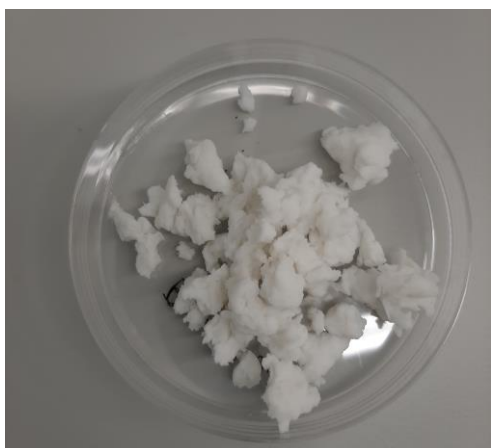


Figure 3. Starting material cellulose nanofibril water paste in Petri dish.

CNF was stored in tight container in fridge to minimize water evaporation. The polymer matrix bark powder is extracted from side stream of bark waste. It is residue from Finnish cosmetics company Innomost. Hydrophobic bark powder is in dust form.

3.2 Sample preparation

In this chapter the procedure for making CNF and CNF-bark powder films is described. Pure CNF film without bark powder is made as a reference sample to compare the properties of bark powder added films.

CNF film was prepared by grinding the 15 wt% raw material in mortar. 13,51 grams of CNF was weighed in small pieces. It was grinded in small amounts by first grinding the solid mass and then adding small amounts of deionized water (3-5 ml at a time). After the previous piece was grinded more solid was added to the mortar and the process was repeated until all the weighed dispersion was grinded into slush with water. It took approximately 100 ml of water to make homogeneous slush. Water was added into slush until it could be equally poured into two empty 400 ml beakers. Water was added until the volume in both beakers was 400 ml.

When bark powder was added to CNF dispersion the same procedure as for pure NFC film was used but bark powder was added in grinding process. 3 samples with varying bark

powder weight percentage in respect to CNF content were prepared. As CNF comes in dispersion the real mass of fibrils in 13,2 g is approximately 2 grams. Weight of 15 wt% CNF for the films were 13,24 g, 13,22 g and 13,23 g. Films were made with 200 mg, 400 mg and 600 mg bark powder additions. The samples are 10-, 20-, and 30 wt% of bark powder with respect to NFC solid content in sample respectively. Bark powder was added in small amounts at a time and grinded with NFC (figure 4).



Figure 4. Nanofibrillated cellulose and bark powder grinded with deionized water.

Each suspension was grinded approximately equally. Visible agglomerates were grinded as shown in figure 4. However, nanoscale agglomerates may exist making it difficult to grind the suspensions to exactly the same degree.

The following steps were carried out in a fume hood. Two beakers at a time were transferred to TIMCO ultrasonic bath (figure 5). The samples were sonicated for 30 minutes. Sonication is done to deagglomerate and homogenize nanocellulose suspension (Hoo et al., 2022). This is the second step after grinding to make the fibrils separate from agglomerates.



Figure 5. Timco ultrasonic bath. NFC suspension in two 400 ml beakers in sonication.

After sonication the suspension was vacuum filtered. Vacuum pump, ceramic Buchner funnel, Bucher flask, rubber bung, filter paper (diameter 12,2 cm), and rubber tubes are needed to establish the vacuum filtration set up. Process is shown in schematic figure 6. Vacuum filtration directs the fibrils in horizontal plane, and it is used to dewater the paper (Sethi et al., 2021).

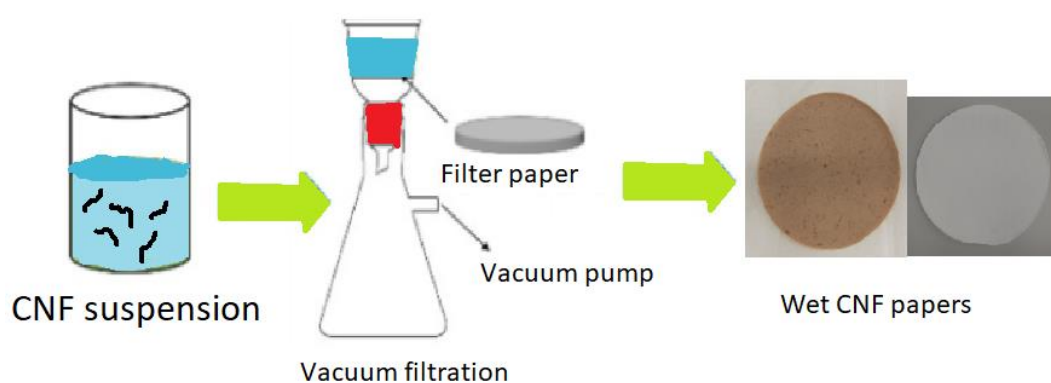


Figure 6. Schematic of CNF paper preparation

Filter paper was moistened with deionized water before sonicated dispersion was poured on the paper. Small layer of suspension was poured on the paper and the vacuum pump was switched on. More dispersion was added on the funnel when there was space. After water drops were not dropping, pump was 10 minutes on to yield in optimal filtration result. Filter paper and wet NFC paper were removed carefully from the funnel with a metal spatula. Papers were drying for 24 hours under a dish filled with water as a weight to remove wrinkling of the paper. NFC composite papers were in between paper towels so that they did not have direct contact with the dish. After 24 hours, weight was removed, and paper was drying in a fume hood for another 24 hours. After that, the films were dry, and they were stored five days in a room temperature storage in an open plastic bag until pressing. Filter paper was removed before further processes.

3.2.1 Pressing

For analytical measures the film should be flat. For that purpose, Techlab Systems Pneumatic TAPPI PRESS model NPT-10 was used (figure 7). Usually, NFC film is wet pressed after vacuum filtration (Sethi et al., 2021) but in this experiment, the film was pressed when it was dry, since the purpose was to leave the film's surface rougher than it would become by wet pressing. Roughness was expected to increase hydrophobicity.



Figure 7. Techlab Systems Pneumatic TAPPI PRESS model NPT-10 for wet pressing papers.

Standard ISO3688:1999(E) (Pulps-Preparation of Laboratory Sheets for the Measurement of Diffuse Blue Reflectance Factor (ISO Brightness)) was used. Sample was in between plates and moisture absorbing arcs. The pressure was 6 kg/cm^2 and pressing time was 1 minute. The films were pressed twice because the outcome was not expected after the first time; the film did not straighten properly. After pressing for two times the result was acceptable but had unwanted corrugation. The preparation of specimens for characterization is discussed in the following chapters.

3.3 Analysis/characterization

In this chapter analysis methods and procedures are explained. The importance of each method is explained.

3.3.1 Tensile strength

Tensile properties of the composites were characterized with Shimadzu AG-IC universal testing machine, equipped with 100 kN load cell. Rectangular $50 \times 60 \times 5 \times 0,5 \text{ mm}^3$ specimens were cut from pressed pure NFC and composite films. 5 samples were made from each of the 4 papers. For UTM machine samples had to be prepared with holders. Single wall corrugated cardboard was used. Both ends of the samples were glued in between two quadrangles of cardboard with hobby glue. 30 mm was set as the gauge length; therefore, cardboards were glued so that 30 mm of sample would be between jaws of the UTM machine. Gauge length is the distance between the edge of the upper and lower jaws. Schematic of the specimen is shown in figure 8.

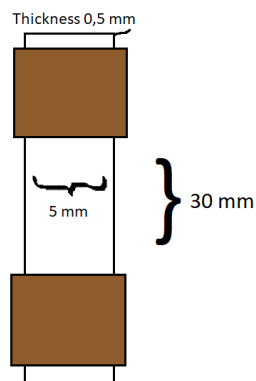


Figure 8. Schematic of the specimen size for tensile testing.

For tensile testing, the gauge length was set at 30 mm. A testing speed of 5 mm/min was used. Test mode was “Single”, test type was “tensile”, capacity of 100 kN and control mode was “Stroke”. Maximum force, stress, stroke, and time were recorded. Maximum stress tells the tensile strength and maximum stroke what the longest elongation was. Five specimens were tested for each material.

Each sample was stored in same laboratory conditions. Samples were cut in random direction since the film should be homogenous, fibres are randomly oriented due to sonication (Nissilä et al., 2019). Samples are shown in figure 9. Numbers on the samples indicate the relative weight percentage of bark powder to NFC dry mass. Generally, specimens for UTM machine are dumbbell shaped to promote fracture in the monitored region (AHSS Guidelines).



Figure 9. Specimen for tensile testing. Upper row 5 specimen for pure NFC paper and 5 specimens for 10 wt% bark powder/NFC paper. Lower row 5 specimen for 30 wt% and 5 specimens for 20 wt%.

Graphical results were obtained with the control computer software that was connected to UTM machine. Results are shown in 4.2.

3.3.2 Field Electron Scanning Electron Microscope (FE-SEM)

After tensile tests, one specimen from pure, 10 wt% and 30 wt% series of 5 parallel samples were chosen for analysis with FE-SEM. Fracture surface resulting from UTM shows the breakage point of fibrils and is therefore suitable for FE-SEM. Image of 20 wt% sample was not analysed since the number of samples was limited.

The samples for FESEM were prepared by sputtering platinum on the fracture surface of the NFC film, 10 wt%- and 30 wt%- bark powder/NFC composites that were obtained from UTM mechanical tensile testing. Jeol JSM-7900 F was used to examine the morphology of the materials. FE-SEM results give important information about particle integration.

3.3.3 Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR)

Attenuated total reflectance Fourier transform infrared analysis was carried out to acquire information about chemical bonding and functional groups in the films. Interfacial interaction between bark powder and NFC can be investigated. FTIR spectrum was produced with Bruker Alpha-P instrument using diamond tip in attenuated total reflection (ATR) mode. The range was set $400\text{--}4000\text{ cm}^{-1}$. The resolution was: 4 cm^{-1} and scan number 128.

$0,5\text{ cm} \times 0,5\text{ cm}$ piece of each sample was investigated in ATR mode. Reference sample (pure NFC) and bark powder are analysed as well. Morphological characters of modified NFC (composite films) give important details about the chemical properties of the material.

3.3.4 Wide angle X-ray scattering (WAXS)

WAXS study was carried out for each of the four different papers. Trapezoidal $2,5\text{ cm} \times 2,5\text{ cm}$ specimens were cut from each material (figure 10), and they were placed tightly on the

sample holder to avoid the influence of corrugation on the reflection angle. Corrugation is visible in figure 10; the samples don't stay even on the table but rather some edges curve. The target is to analyse d-spacing which will give important information about integration of bark powder within NFC crystal domain. D-spacing is calculated using the Braggs equation.



Figure 10. Specimen for WAXS analysis. Increasing bark powder content from left to right.

Copper pipe was used. Voltage was 40 kV and current 40 mA. Optic was “Fixed sample illumination” and the measuring area was 12 x 20 mm. The angle range was 5–70 degrees with an increment of 0,025 degrees. Intensity was 0,3 and the sample rotated 10 revolutions per minute.

3.3.5 Water contact angle

Hydrophobicity is one of the required properties of polymer composite materials. Composites are used in numerous environments and therefore they need to sustain humidity and moisture well. (Doughett & Asnarez, 2010; Gribniak, 2021) Therefore it is important to study contact angle to characterize the surface properties of bark powder/NFC composite.

The larger the value of contact angle θ , the greater is the hydrophobicity. Materials with $\theta < 90^\circ$ are considered hydrophilic. Materials with $\theta > 150^\circ$ are referred as superhydrophobic materials. One of the most common methods for determining contact angle is sessile droplet method (Volfkovich et al., 2022). In this method, a water droplet is applied on a horizontal flat surface, photographed, and the contact angle is determined from the profile of the droplet with an external program (De La Madrid et al., 2019).

The contact angle was determined with KSV Instruments CAM 101. Images were taken with a digital camera (Imaging source model DMK 21F04) at room temperature. Analysis was carried out with the software provided by the instrument manufacturer. Measurement method was “Static”. 3 still images were taken with fast frame interval of 165 ms. Fitting method was Young/Laplace. A drop of $\sim 3.5 \mu\text{L}$ ion exchanged water was placed on the surface of a specimen with KSV Instruments syringe. The contact angle and droplet volume were measured. Droplet volume was measured to control the size of the droplet. The result was not accepted if the droplet size differs from $3\text{--}4 \mu\text{L}$. Standard deviation of the parallel measures is evaluated and the homogeneity of the different materials is compared.

Some of the previous studies have given contact angle of 49° for pure NFC film (Layek et al., 2021). However, the process of film preparation and pressing were different so same results are not expected. To the best of our knowledge there is no previous study on contact angle of bark powder/ NFC composite films.

Polyurethane/CNF surface modified nanopaper showed increased angle of 83° from 46° (Sethi, Farooq, Österberg, et al., 2018). Polyurethane is hydrophobic (Sethi, Farooq, Österberg, et al., 2018) as well as bark powder (Korpinen et al., 2022). Increased angles can be expected from bark powder/CNF films compared to pure CNF film.

4 Results and discussion

In this chapter experimental results are presented and the meaning of them is discussed. Each analysis method gave important information about the properties of the new innovative nanomaterial.

4.1 Structure of bark powder/NFC films

Bark powder mixed well with NFC and formed homogenous looking dispersion in grinding phase. However, in ultrasound bath bark powder started separating from NFC. It formed agglomerates, which were tried to split with metal spatula. All the agglomerates could not be dispersed as shown in figure 11. Darker red/brown flakes are agglomerates of bark powder.



Figure 11. Illustration of non-homogeneous dispersion of NFC and bark powder.

The ultra-sonication and vacuum filtration resulted in wet fibrous material. Sample prepared from pure nanocellulose fibrils is white in color as shown in figure 12. Composites prepared from 200 mg, 300 mg and 400 mg bark powder resulted in wood-colored films. The film with 300 mg bark addition is shown in figure 13. The diameters of the wet films were the same as the diameter of the filter paper (12,2 cm).



Figure 12. Wet pure NFC paper



Figure 13. Wet 30 wt% bark powder/NFC composite

In vacuum filtration bark powder agglomerates were formed on the surface of the paper but it is approximated that they didn't affect the mechanical characteristics of the composite. During drying process, the colour of the composite films appeared homogenous unlike in images 11 and 13 above where bark agglomerates are visible.

The average dimensions of the dry films decreased from those of the wet films since water evaporated and the films shrank during drying process. Each of the films wrinkled during drying without weight (figure 14).



Figure 14. Illustration of the wrinkling phenomenon in drying process. White paper is the filtration paper and brown paper is 30 wt-% bark powder/NFC composite paper after completely drying.

Dry material was rough and strong. It could be described as plastic. The drying time was relatively long (approximately 48 hours). Sethi et.al have suggested that slow water removal from CNF suspension might slow the advancement of the material in the field of functional materials (Sethi et al., 2021). Hot pressing could also increase drying speed (Österberg et al., 2013) but as a result the surface would be flatter; in this experiment the intention was to have rougher surface.

4.2 Tensile properties

For applying polymeric films in structural composite applications excellent mechanical properties including mechanical strength and ductility are required. Therefore, it's crucial to investigate bark/CNF composites's mechanical properties. Mechanical testing was carried out as described in chapter 3.3.1 and the performance of the materials is shown in figure 15 in form of a stress-strain curve.

Tensile force (N) and tensile strain (mm) are represented in the stress strain curve. Blue colour is for pure NFC, pink for 10 wt%, fuchsia for 20 wt% and orange for 30 wt% bark powder / NFC composite. X-axis shows elongation (stroke) and y-axis force. Blue dots are the maximum force that each different material could bear until breakage. Tensile strength is given in MPa, which is converted from maximum breakage force estimating that cross-sectional area is rectangular (2.5 mm²).

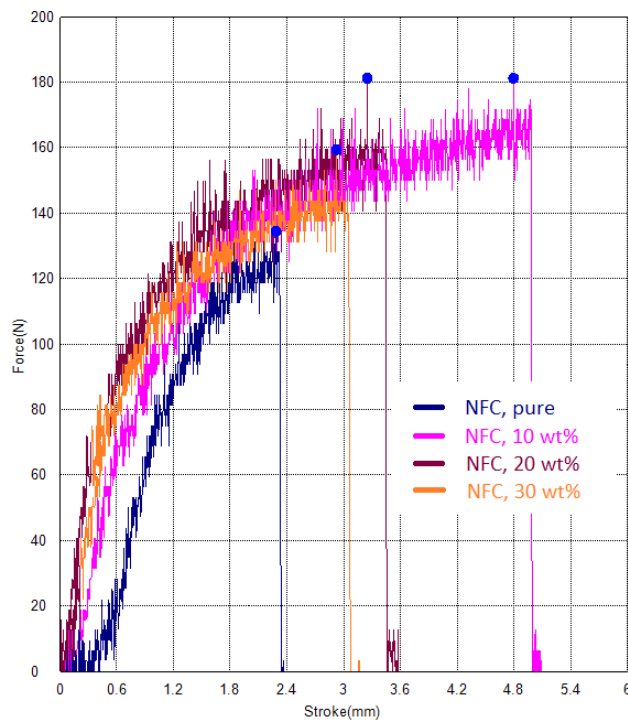


Figure 15. Tensile testing diagram for pure NFC and 3 bark powder/NFC composites.

Only 1 out of 5 data for each set of parallel samples is presented here. Cellulose nanofibrils (CNF) is an interesting nanopaper composite material with an excellent mechanical strength of 54 MPa. That is one of the reasons why CNF film has been lately gaining a lot of attention as an ideal alternative for replacing fossil-based polymers in numerous areas like packaging, building and hybrid material research. The high mechanical strength value can be explained by the OH-functional groups on CNF's surface. These functional groups pull the cellulose nanofibrils extremely tightly together via hydrogen-bonding interaction. Because of solid interfacial interaction between the chains of CNF, the produced paper is rigid and less ductile (Abdul Khalil et al., 2012; Eichhorn et al., 2010). Pure CNF paper has elongation at a break of 2.3 ± 0.1 mm.

Modifying pure CNF with bark powder or with one of the many other possibilities such as those discussed in chapter 2.4 can lead to further enhancement of mechanical properties. That can further improve the chances of new nanomaterial to be employed in demanding high quality structural applications and composite laminates. (Eichhorn et al., 2010; Malho et al., 2012)

Figure 15 indicates that integration of bark powder into CNF matrix has increased both tensile strength and stroke for every concentration. For 10 wt% bark/NFC composite tensile strength increased from 54 MPa to 73 MPa. Elongation at break increased from 2.3 ± 0.1 mm to 5.0 ± 0.1 mm. For 20 wt% bark/NFC composite tensile strength was similar than for 10 wt% specimen (73 MPa). However, elongation at break (3.4 ± 0.1 mm) was lower, but higher than for pure NFC. Compared to 20 wt% and 10 wt% papers, 30 wt% composite had lower tensile strength (63 MPa) and stroke (3.1 ± 0.1 mm). NFC is an amphiphilic molecule, which means it has hydrophobic and hydrophilic side. Bark is hydrophobic in nature. Bark powder can interact with hydrophobic site of nanocellulose via hydrophobic interaction. (Malho et al., 2012) Now when bark powder is integrated in between NFC, -OH groups are reserved and might block interaction between NFC fibrils. Therefore, strength and elongation increase. Results are collected in table 1.

Table 1. Results from the mechanical testing; tensile strength and elongation at break.

Sample	Tensile force (N)	Tensile strength (MPa)	Elongation at break (mm)
PURE NFC	135 ± 3	54	2.3 ± 0.1
Bark/NFC 10 wt%	182 ± 1	73	5.0 ± 0.1
Bark/NFC 20 wt%	182 ± 1	73	3.4 ± 0.1
Bark/NFC 30 wt%	158 ± 1	63	3.1 ± 0.1

The results in table 1 propose that 10 wt% bark/NFC composite has the best mechanical properties of the 4 materials studied. 20 wt% paper has same tensile strength but is less ductile (smaller stroke) than 10 wt%. 30 wt% paper has slightly better properties than pure NFC.

Generally, integration of fillers (like bark powder) into NFC (polymer matrix) hinders the polymer chain's motion segmentally and therefore composite paper's mechanical strength is increased but ductility is decreased. However, from the experimental data it can be seen that integration of bark powder simultaneously enhanced both tensile strength and elongation. That could be explained by the nanoscale integration of filler into NFC matrix that is amphiphilic (Eichhorn et al., 2010).

Bark powder integrates with nanocellulose fibrils via hydrophobic interaction. Load is transferred from bark powder to CNF matrix which possibly enhances the mechanical strength of bark/NFC composite. Few -OH groups are blocked for H-bonding interaction with adjunct cellulose units when hydrophobic material (bark powder) is integrated to NFC matrix. (K. Y. Lee et al., 2014) Decrease of H-bonding activity can bring more ductility and flexibility in bark/NFC composite compared to pure NFC film (K. Y. Lee et al., 2014; Nishiyama, 2018).

It was expected that tensile strength and elongation at break would increase with the increase in bark powder concentration in CNF matrix. Results however suggest that ductility and mechanical strength of bark/CNF 30 wt% composite decreased compared 10 and 20 wt% composites. However mechanical properties increased compared to pure paper. Dispersity of the filler into matrix impacts the mechanical properties of composite material (Shalan et al., 2021). Mechanical behaviour can only be good if appropriate dispersion is achieved (Sethi et al., 2021). Scientists have reported weakening effects of agglomerating of filler particles on mechanical properties since filler/matrix interaction is reduced (Corrêa et al., 2006; Leprince et al., 2010). FE-SEM images of dispersion give more evidence of agglomerating in the following chapter.

For experiment to be successful the sample should break around the middle of the rectangle. Figure 16 shows the breaking line of each sample. Pure NFC samples fractured ideally. White samples in the left upper corner are pure NFC. Some of the composite samples fractured unideally either from the upper holder or lower holder. That can be seen for 30 wt% samples in the lower left corner. First two samples broke from the bottom holder and the third sample broke from the upper holder. The fourth and fifth samples of 30 wt% NFC fractured well.

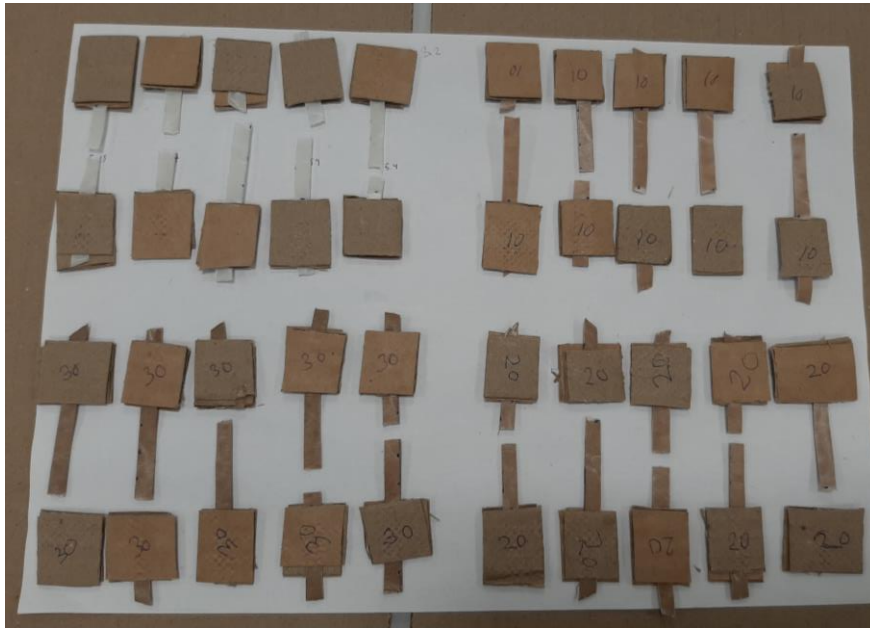


Figure 16. Fracture lines of each specimen.

When water drains, bonding in nanocellulose reaches critical distance where the van der Waals force and the hydrogen bonding produce an aggregate. Nanopaper is produced by a layer-by-layer deposition. Outstanding mechanical properties of the nanopapers are due to this condensed morphology. (Sethi, Farooq, Sain, et al., 2018)

4.3 Morphology

Results from the morphology studies are presented below. Three analytical instruments were used to obtain information about the morphology of the composite.

4.3.1 FE-SEM study

Mechanical behaviour can only be good if appropriate dispersion is achieved (Sethi et al., 2021). FE-SEM was carried out to investigate the dispersion of bark powder into NFC matrix and resulting FE-SEM images of pure NFC and bark powder/NFC composite paper are shown in figures 17, 18 and 19 below.

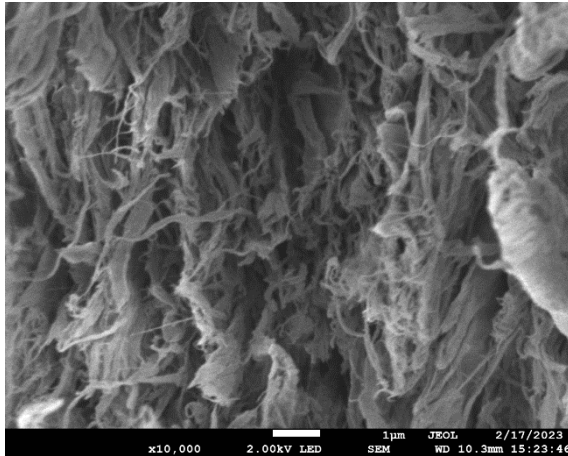


Figure 17. FE-SEM image of pure NFC.

Pure NFC has fibrillated layer structure. Vacuum filtration orientates fibrils horizontally on top of each other in numerous nanoscale layers (Sethi et al., 2021). Fibrils can be seen in figure 17. Many fibrils are assembled to produce bundle-like fibrillar structure and do not therefore appear single fibrillated structure.

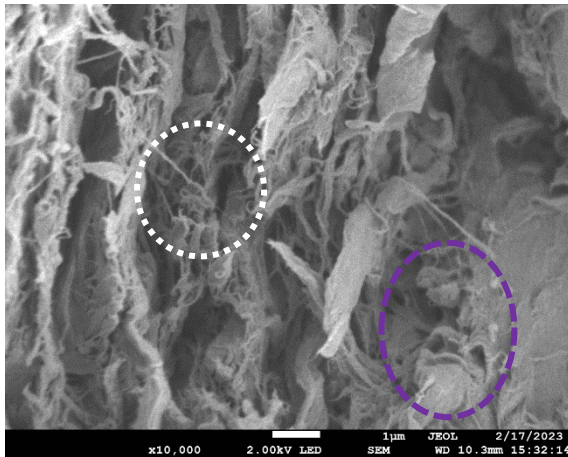


Figure 18. FE-SEM image of 10 wt% bark powder/ NFC composite

In figure 18, 10 wt% bark powder/NFC composite shows well dispersed bark powder in NFC matrix with some agglomerates that are presented in purple circle. White circle points site of appropriate dispersion.

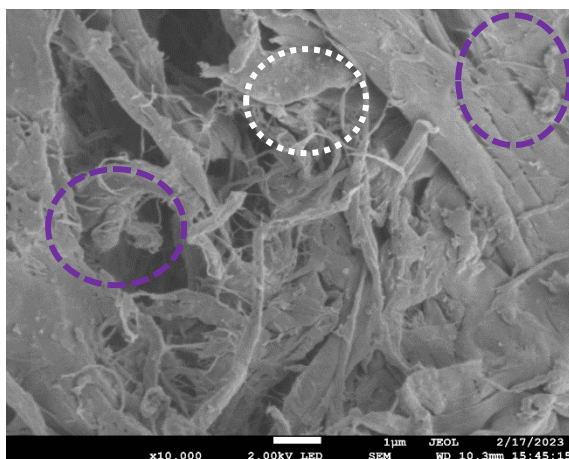


Figure 19. FE-SEM image of 30 wt% bark powder/ NFC composite

In 30 wt% composite there are many agglomerates of bark powder. Bark hasn't properly dispersed into NFC matrix. Purple circles show bark powder agglomerates in 30 wt% material. That could explain the decrease in mechanical properties as explained in chapter 4.2. Agglomerating might be caused by high interaction among bark powder particles (Nishiyama, 2018; Sethi et al., 2021). At agglomerated points there is a different structure of material, and those points bear stress differently than composite material. Therefore, it may affect mechanical properties negatively (Leprince et al., 2010). Elongation at break of 30 wt% composite decreased 13,2 % and tensile stress 8,8 % compared to 20 wt% composite, which according to FE-SEM images could be due to inhomogeneous composite material that results in inhomogeneous stress transfer through the material making the paper more brittle.

4.3.2 ATR-FTIR study

ATR-FTIR study was carried out to investigate the effects of interactions of bark powder with nanocellulose fibrils. It is important to study how the peak position is shifting in the bark/NFC composite film with respect to NFC since it will explain the research question of compatibilization chemistry and bonding between NFC and bark powder. This interaction will also help to explain the mechanical behavior of bark/NFC composite. FTIR spectrums are displayed below in figures 20, 21, 22, 23 and 24.

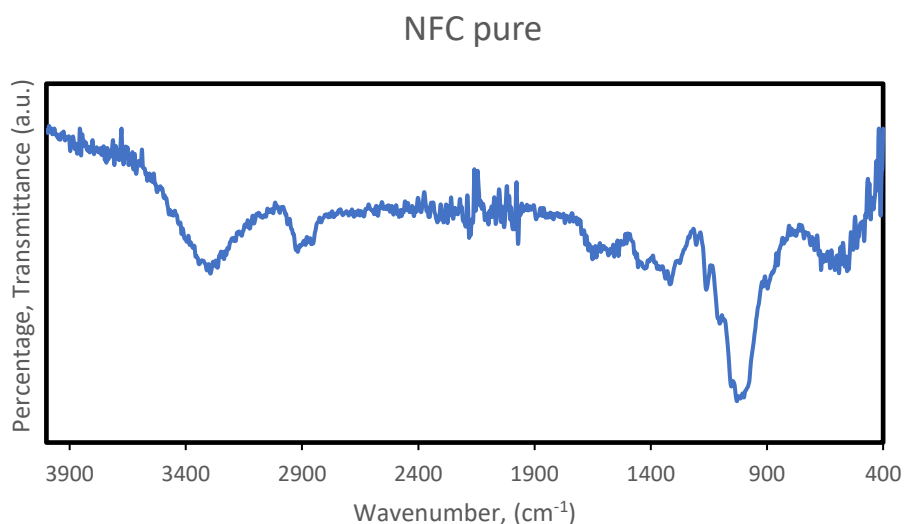


Figure 20. FTIR spectrum of pure NFC in range 400–4000 cm⁻¹.

Pure NFC has broad stretching vibration -OH band around 3500–3300 cm⁻¹. Peak at 2900 cm⁻¹ indicates C-H stretching vibration. Sample has numerous cellulose units which have SP³C-H groups. Peak at 1650 can be recognized and it indicates -OH stretching vibration of associated water molecule in NFC. (Haafiz et al., 2014) The peaks located at 1460–1410 cm⁻¹ are indication of -CH₂ vibration and C-H stretching which assign the crystallinity of cellulose (Trache et al., 2014). Intense peak group around 1200–900 cm⁻¹ could prove the existence of -OH bending, C-O-C symmetric bonding and C-O stretching (Li et al., 2021). The peaks are gathered in table 2.

Table 2. FTIR spectral peaks for nano fibrillated cellulose

Band, [cm ⁻¹]	Functional group
3600–3300	OH- stretching
2900	CH- stretching vibration
1650	OH- stretching vibration (associated water)
1400	CH ₂ -vibration
1150–1050	CO- stretching
1060–1070	C-O-C- stretching

Each peak in table 2 are characteristic for nanocellulose (Hu & Hsieh, 1996; Trache et al., 2014). The spectrum for bark powder is shown below in figure 21. The spectrum has many similarities with FTIR spectrum for lignin (Nandanwar RA et al., 2016) and castor bark powder (De Mendonça Santos et al., 2017) . Bark powder is from cosmetics company Innomost and the specific content of the powder is not known. Pinto et al. reported that the outer bark of silver birch consists of 45% suberin, 40% extractives, 9% lignin, 4% hemicelluloses, and 2% cellulose, on average (Pinto et al., 2009).

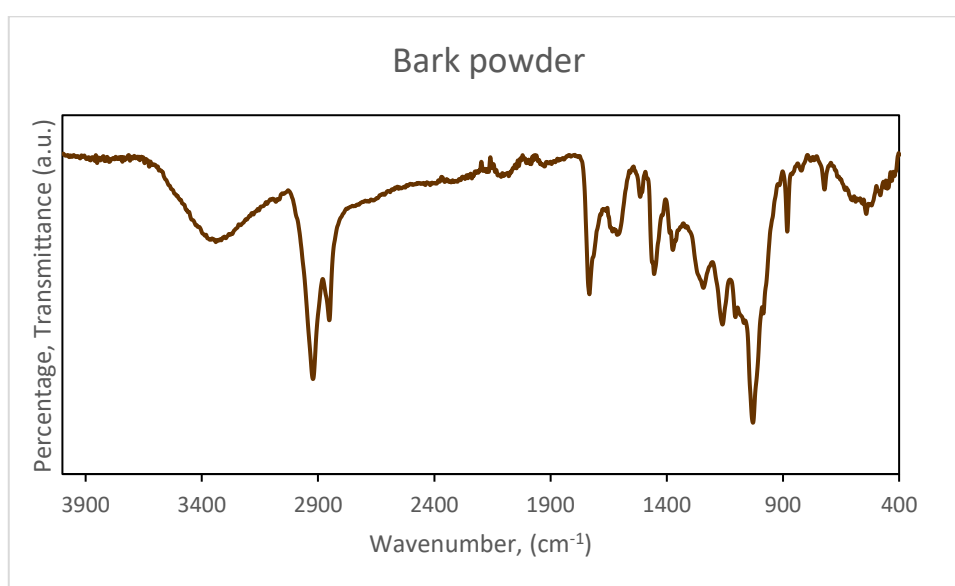


Figure 21. FTIR spectrum for bark powder.

Figure 21 shows the FTIR spectrum of the bark powder. The wide peak centred at 3400 cm⁻¹ is indicating presence of OH group from lignin or suberin. Absorption peak at 2900 cm⁻¹ is assigned to C-H stretching. (Li et al., 2021) High intensity of the peak indicates that long chain C-H-compounds like lignin and suberin are detected (Grassino et al., 2016; Pinto et al., 2009). The band around 1600 cm⁻¹ is indicating carbonyl group CN or C=O from carboxylates, as carboxylic acids might be present in Innomost's bark powder composition (Korpinen et al., 2022; Pinto et al., 2009). The functional group C-O can be identified from the intense band at 1050 cm⁻¹ (Korpinen et al., 2022). FTIR spectra for composites are shown below.

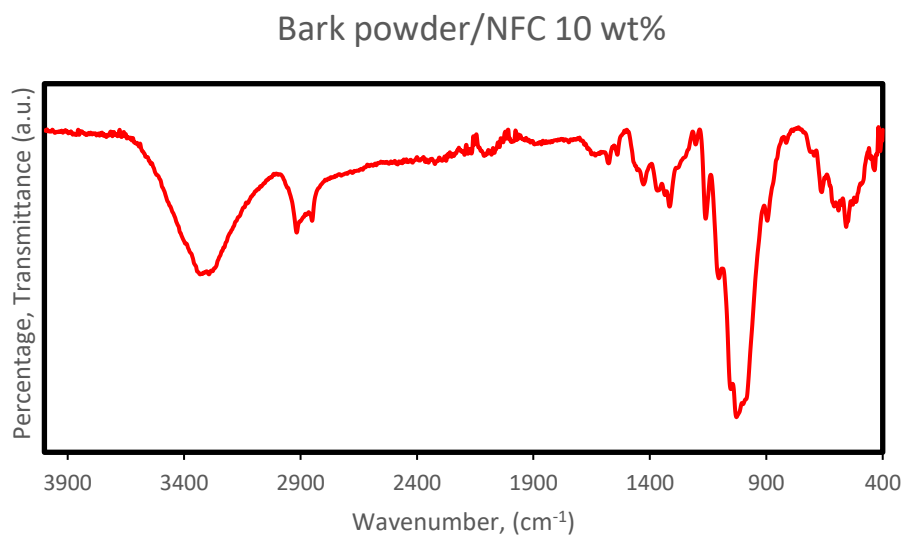


Figure 22. FTIR spectrum of 10 wt% bark powder/NFC composite in range 400-4000 cm⁻¹.

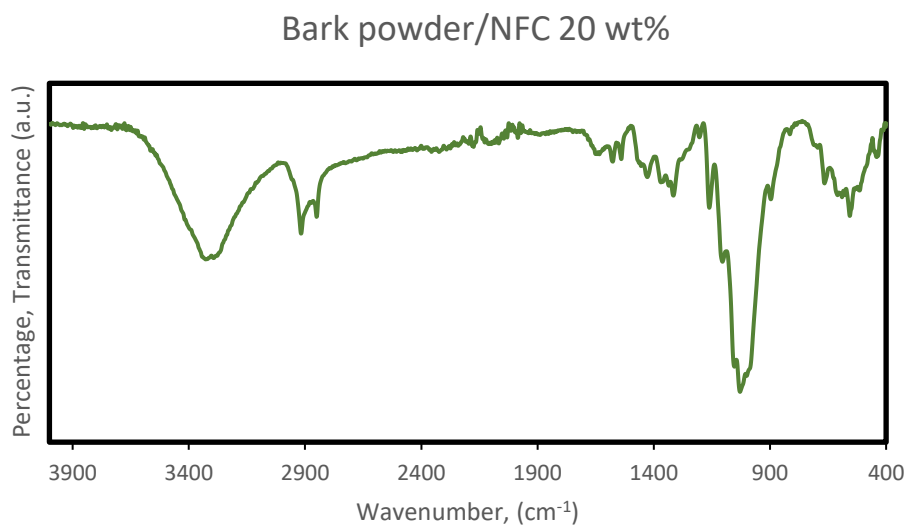


Figure 23. FTIR spectrum of 20 wt% bark powder/NFC composite in range 400-4000 cm⁻¹.

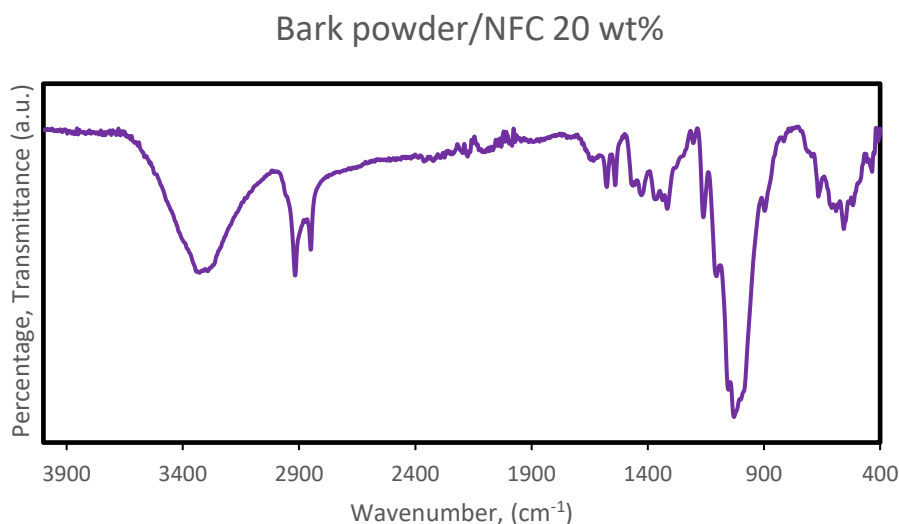


Figure 24. FTIR spectrum of 10 wt% bark powder/NFC composite in range 400-4000 cm^{-1} .

Each spectrum has visible -OH band around 3000-3500 cm^{-1} . That is expected since both pure NFC and bark powder have -OH groups in their structure. Spectrum for each composite is very similar. Same peaks are present in each spectrum. Notable changes are about the peak at 2900 cm^{-1} . The peak intensity increases when bark powder content is increasing. Pure bark powder has the most intense 2900 cm^{-1} peak. Absorption peak at 2900 cm^{-1} is assigned to C-H stretching (Li et al., 2021). Higher intensity of the peak indicates that more long chain C-H-compounds like lignin and suberin are detected (Grassino et al., 2016; Pinto et al., 2009). That is reasonable when more bark powder is present. Combining bark powder and NFC gives combined FTIR spectrum. There is minor shifting of transmittance bands and therefore it is difficult to comment about interaction happening between nanocellulose and bark powder. Band locations of -OH band, C-O/C-O-C-band and C-H stretching are shown in table 3.

Table 3. Band locations for selected peaks in FTIR spectra for pure, 10 wt%, 20 wt% and 30 wt% composites.

	-OH band, [cm⁻¹]	C-O, C-O-C stretch, [cm⁻¹]	C-H stretching, [cm⁻¹]
Pure	3295	1030,4	2920
10	3295	1030,4	2918
20	3324	1030,4	2918
30	3313	1028,3	2918

Table 3 indicates that minor shifting of FTIR bands take place. Most shifting is visible for OH- stretching band. The tips of the peaks are located in the range 3324-3295 cm⁻¹. C-O- stretching peak is same for all the materials except 30 wt% composite. C-H- stretching band for composites is at same location but 2 cm⁻¹ different for pure NFC.

4.3.3 WAXS study

Structure of bark powder/CNF composite papers was studied with wide angle X-ray diffraction scattering from angle 2θ=5- 70°. Also reference sample (pure CNF) was analysed. Resulting diffractograms from WAXS are shown in figure 25.

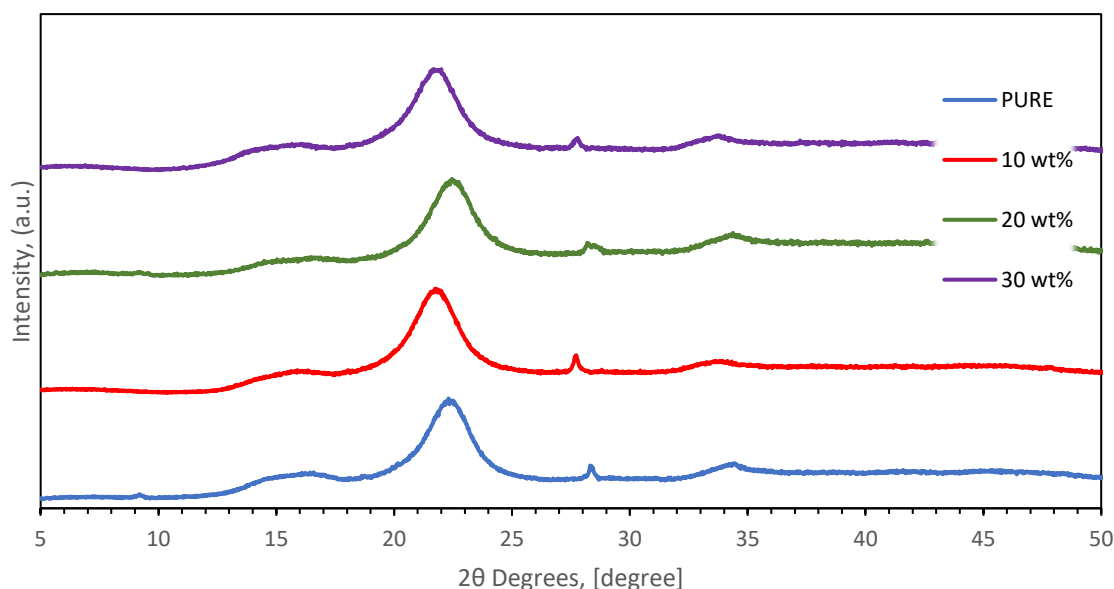


Figure 25. WAXS diffractograms of pure CNF, 10-, 20- and 30 wt% bark powder/CNF composites.

Five peaks from diffractogram for pure CNF are detected in range $2\theta=5-40^\circ$. Cellulose nanofiber is not purely crystalline material as the structure has some disordered domains. Crystalline and amorphous regions are distinguished in CNF diffractogram. (H. V. Lee et al., 2014) Intense peak centred around 22.4° represents crystalline domains (polymorph type 1) of CNF (Park et al., 2010). Broader peak around $16-17^\circ$ represents the amorphous domains of CNF (Mohd et al., 2016).

Diffractogram shows that all the specimens have most intense peak at 22.4° which is typical for natural cellulose. It is denoting that highly crystalline regions are present. (Mohd et al., 2016) Significant peaks were identified around 16.4° , 22.5° and 34.6° 2θ -diffraction angles (figure 25). These peaks are associated with (110), (200) and (004) planes of cellulose respectively (Kumar et al., 2013; Mohd et al., 2016; Park et al., 2010). There are two different crystal structures (triclinic and monoclinic) (Park et al., 2010). Both are present but monoclinic peak is more intense.

For pure NFC there is minor peak at around $2\theta=9.2^\circ$ which corresponds to repeating unit of trimethylglycine. Each diffractogram has minor sharp peak around $2\theta=28^\circ$. Peaks around 28° correspond to non-removed hemicellulose in NCF matrix. Non-removed hemicelluloses decrease the crystallinity of the material because they are amorphous. (Daicho et al., 2018)

From figure 25 it is noticed that peaks have slightly shifted compared to pure NFC. That addresses a change in crystallinity (Hu & Hsieh, 1996; Park et al., 2010). Distance between NFC crystals change when bark powder or any filler is integrated in the matrix (Daicho et al., 2018). The lattice spacing or d-spacing was calculated using Bragg's equation, equation 1.

$$\lambda = 2d \times \sin\theta \quad (1)$$

where λ is the X-ray wavelength (0.154 nm for Copper pipe (Li et al., 2021)), d is the lattice spacing on the crystallographic planes, θ is the corresponding Bragg angle (Hu & Hsieh, 1996). Lattice spacings are presented in table 4 below. Lattice spacing is not calculated for angle around 28° since other research only report about planes 110, 200 and 004 corresponding to the angles around 16° , 22° and 34° (Ciolacu et al., 2011; Cui et al., 2014; Hu & Hsieh, 1996; Li et al., 2021).

Table 4. Lattice spacing calculated for planes 110, 200 and 004, corresponding to the diffraction angles around $2\theta=16^\circ$, $2\theta=22^\circ$ and $2\theta=34^\circ$.

	110	200	004
PURE	0.545	0.398	0.260
10	0.557	0.408	0.259
20	0.538	0.396	0.260
30	0.550	0.410	0.266

Table 4 presents the d-spacings calculated from Bragg's equation. Values for 110 and 200 planes are similar that Li et al. have reported (Li et al., 2021). Generally, it can be noticed

that d-spacing values are increasing when bark powder content increases. That means that powder is integrating with NFC matrix. However, for 20 wt% composite d-spacing values are smaller than for pure NFC meaning shifting to other direction. That is an indication that integration has not occurred ideally. Another challenge with WAXS was corrugation of composite papers. Specimen should be completely flat for WAXS in order to radiation interacting with the plane properly. However, our samples were wrinkling, and it was challenging to set them straight on the sample holder.

Obtaining data from chemical bonding and crystallinity structure is important for further application and designing nanocellulose-based materials at the molecular scale (Martin-Martinez, 2018). Ciolacu et al. report that smaller d-spacing indicates a stronger hydrophobic interaction (Ciolacu et al., 2011). Increasing d-spacing reveals that the intermolecular force between nanocellulose fibers is decreasing, meaning that bark powder is integrating to the matrix (Cui et al., 2014).

4.4 Water contact angle

To investigate the hydrophobicity of the bark powder/NFC composite, the sessile water droplet contact angle was performed. 8 parallel measurements were carried out for pure NFC, 10-, 20-, and 30 wt% bark powder/NFC composites. Each droplet was applied on a unoccupied spot as shown in figure 26, and the image was analysed.

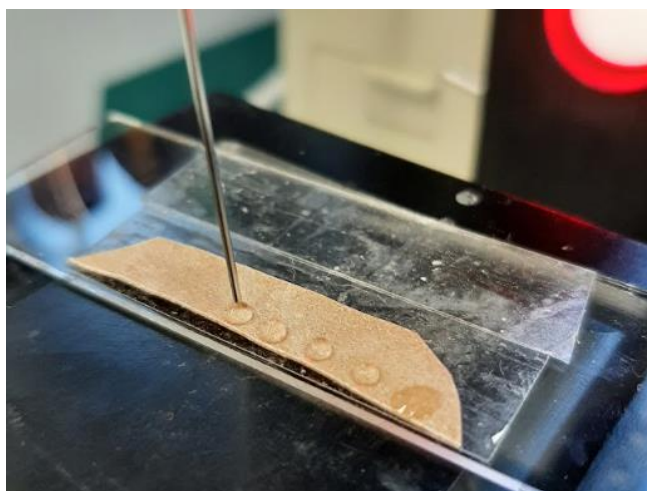


Figure 26. Water contact angle measurement for a specimen of 30 wt% bark powder/NFC composite.

Figure 26 shows four successfully dropped water droplets and one that was absorbed by the material. Absorption phenomenon happened only a few times, mostly for 30 wt% composite. Specimens were straightened by hand before placing on the analysis plate. That might have caused minor cracks or something comparable which create inhomogeneous point for water to absorb in. Absorbed droplets were not considered in the calculations. Results are shown in table 5.

Table 5. Average contact angle and standard deviation from 8 parallel measures for each material.

Sample	Average contact angle [°]	Standard deviation
Pure NFC	78,98	9,92
Bark/NFC 10 wt%	88,10	7,64
Bark/NFC 20 wt%	100,91	6,47
Bark/NFC 30 wt%	94,13	6,75

Pure NFC shows a contact angle of 78,98° indicating that it is hydrophilic in nature. Contact angle under 90° is associated with hydrophilic materials (Douville, 2004). Our NFC paper has rough surface due to pressing after drying. Other researchers have reported lower contact angles for pure NFC: 46° (Sethi, Farooq, Österberg, et al., 2018), 49° (Layek et al., 2021) and 24° (Sehaqui et al., 2014). The surfaces of their papers were smoother due to different pressing procedure. Smoother surface is naturally more hydrophilic (Tamai & Aratani, 1972). Due to the integration of hydrophobic bark powder into NFC matrix and surface, the water contact angle values increased from 78,98° to 88,10° for 10 wt% composite, to 100,91° for 20 wt% composite and to 94,13° for 30 wt% composite.

Standard deviation is similar (around 7) for composites but slightly higher for pure NFC. There was slight variation between the parallel measurement results for each material. However, angles were $\pm 10^\circ$ from the average of the set. Water droplet volumes were in the range $3,6 \pm 0,4 \text{ mL}$. For more accurate data water droplet volume should be the same throughout the experiment.

It is reported that bark powder is hydrophobic (Korpinen et al., 2022) and therefore, successful integration of bark powder increased the hydrophobicity of bark powder/NFC composites in this study. Increase in hydrophobicity was nearly linear until increasing bark content to 20 wt-%. From the table 3, an increase of roughly 10° is noticeable for bark content increase of 10 wt%. The results indicate that adding bark powder indefinitely doesn't make the material more hydrophobic since 30 wt% composite has lower contact angle than 20 wt%. However, it is higher than that of pure NFC or 10 wt% paper. More data points are needed to find the optimal bark powder content considering hydrophobicity. From the data obtained it can be said that 20 wt% composite is the most hydrophobic. Figure 27 shows one of the 8 droplets set on the film's surface through the camera.

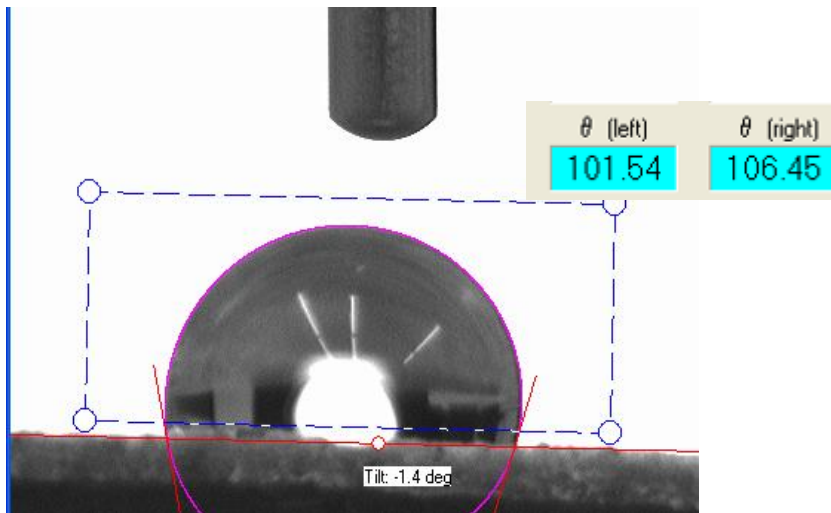


Figure 27. Water droplet set on 20 wt% composite's surface.

Because the specimens were not completely flat, contact angle measurement had difficulties. The camera and objective of the contact angle apparatus are sensitive. The specimen should be flat to avoid corrugated background which can lead to misinterpreted contact points of the droplet and the investigated material. Measurements for each different material was repeated 8 times to minimize the effect of inhomogeneous corrugation on surface. Corrugation can be seen on figure 26; specimen is not glued ideally to the double-sided tape – the edges are wrinkling while the material should be completely flat. Sehaqui et al. has also reported that achieving a reliable contact angle on cellulose nanofilm is a demanding work (Sehaqui et al., 2014).

5 Conclusions

This research aimed to study environmentally friendly biodegradable composite material made from sustainable materials cellulose nanofibrils and bark powder. Nanocellulose has a combination of outstanding properties suitable to produce strong, flexible, light, and green composite material for ever-growing range of applications such as construction, transportation, and electronics.

Sustainable development is becoming the leading concept of businesses and governments alike. The draining of fossil reserves and impacts of global warming, eventually force us look for renewable resources to fill the demand for materials. Population is growing and more construction is needed as well as transportation. Cellulose as inexhaustible source and with outstanding properties could be leading the development. Cellulose nanofibres have an exciting potential as reinforcements in nanocomposites. Due to their nanoscale size and the capability for surface modification, there is great potential to be used for applications in any field.

Experimental study accompanied with the literature review gave us better understanding on the field of cellulose nanofibril based composites. Answer for the research questions were found. Material produced by bark powder integration to NFC made the material hydrophobic. For question about strength and ductility it can be said that tensile properties of NFC increased when bark powder was integrated. The composite with 10 wt% bark powder showed the best mechanical characteristics. Answer for chemistry of compatibilization is that the bonding and interaction between hydrophilic NFC and hydrophobic bark powder is strong and it varies depending on the weight percent. WAXS diagram shows that changes in NFC crystal lattice happen when bark powder could block hydrophobic sites of CNF for interaction between fibrils. Change in hydrophobicity and ductility are caused by the integration of bark powder to CNF matrix which modifies the bonding and structure. Other compounds such as epoxy, graphene oxide and polyurethane could be added to nanocellulose instead of bark powder. Nanocellulose-bark powder composite could replace oil-based plastics, but some more research is needed since this is the first research based on NFC/bark powder composite.

Slow processing time is currently limiting the scale up of NFC paper, but research has been increasing and novel methods are found to fasten the process (Österberg et al., 2013; Sethi et al., 2021). Nanopapers are prepared in small scale because the size is mainly limited to the size of the filtration funnel. Further research is needed to develop machinery for larger scale production of NFC papers for variety of applications and further processes. We also need enhanced understanding on how to minimize the wrinkling and possible structural changes in drying process. Wet-pressing could be used but the benefit of rough-surface is lost.

Another obstacle of successful commercialization of NFC composites is the giant energy consumption that happens when mechanically disintegrating the fibers into nanofibers. Promising pre-treatment methods have been found but more research is needed to decrease the energy consumption significantly in larger scale.

Promising structural materials has been achieved by combining nanocellulose and other components like bark powder in this study or epoxy and graphene oxide in former studies. Selection of filler material for NFC matrix is important since resulting composite should have outstanding properties of hydrophobicity, mechanical strength, flexibility etc. Novel materials should have the same exceptional properties as the materials they are replacing (plastics, metals, glass). Therefore, it is crucial to carry out studies to get convinced about the safety and suitability of the novel materials. Behaviour of nanocellulose itself is relatively well known and explained by its strong hydrogen bonding network. However, the network is changed when filler materials are introduced.

Bark powder/NFC composites proved high mechanical strength. Mechanical strength of 10 wt% bark/NFC composite increased from 54 MPa (pure NFC) to 73 MPa. Elongation at break increased from 2.3 ± 0.1 mm to 5.0 ± 0.1 mm. 20 wt% bark/NFC composite also showed increased tensile strength (similar than for 10 wt% specimen). However, elongation at break (3.4 ± 0.1 mm) was lower compared to 10 wt%, but higher than for pure NFC. Compared to 20 and 10 wt% papers, 30 wt% composite had lower tensile strength (63 MPa) and stroke (3.1 ± 0.1 mm).

Mechanical results were accompanied by morphological study. FE-SEM images of materials showed higher agglomerating of bark powder in 30 wt% composite than 10 wt%. Agglomeration has been reported to weaken mechanical properties since stress is not homogeneously transferred (Corrêa et al., 2006). ATR-FTIR study shows that composites have peaks both from neat CNF and bark spectra. Peak indicating long-chain carbon compounds (e.g., hydrophobic suberin or lignin) increased when bark powder content increased. OH-peak was also clearly visible for each material.

Results from WAXS indicate that changes in crystallinity take place. Bark powder has integrated to the NFC matrix and modified the lattice slightly due to different interactions and forces between molecules. Interaction is changed by the amount of filler in the matrix. Integration also affects how well lattice is modified. D-spacing values indicate that 20 wt% composite has weaker integration than other composites. However, results are influenced by the fact that film wasn't flat on the sample holder so in- and outcoming radiation did not necessarily travel correct distances. Corrugation was the major problem in this study.

From sessile drop analysis expected results were obtained. Since CNF is hydrophilic it had lower contact angle than composite papers. Bark powder is hydrophobic so adding bark powder to the matrix increased the hydrophobicity. Each of the composites had increased hydrophobicity compared to pure NFC. However, 30 wt% composite had lower contact angle than 20 wt% composite. It could be due to agglomerating of bark powder. Or it is an indication that hydrophobicity won't increase indefinitely despite bark powder addition.

It is expected that the research on nanocellulose-bark powder composites will gain more attention in the near future. Possibilities of bark powder are currently underestimated as large amount of bark goes to energy production while it could be used as a green chemical (Holmbom, 2019; Pásztor et al., 2016). Study about the properties of different bark powders i.e., birch, spruce, juniper or aspen could be interesting. Composites could be made with different ratios of various tree species and optimal concentrations could be found.

We saw that in order to achieve enhanced mechanical properties for nanocomposites, excellent filler-matrix interaction is necessary. Hydrophilic nanocellulosic materials have

compatibility problems with hydrophobic matrices, but it has been proved that hydrophobic and hydrophilic material can be combined to form a novel material with outstanding properties. Yet there are many obstacles to tackle and consequently research is required on environmentally friendly modification methods, in addition with understanding of the reactions that appear at the interface of nano fibrillated cellulose polymer matrix and filler.

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