Production of novel cellulosic materials from tropical plants

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1. Introduction

The Philippines' poor implementation on Solid Waste Management Act of 2000 otherwise known as Republic Act 9003 have led to country's serious problem on plastic wastes. During rainy season, plastic wastes can be seen widespread in rivers, lakes and other bodies of waters particularly in major cities. Legislative measures and local ordinances have been implemented to drastically reduced the consumption of non-biodegradable single used plastics. Last July 2021, House Bill 9147 has been passed with the aim to protect life, both land and water, from hazards posed by plastic pollution and to ensure that non-biodegradable single used synthetic plastic products do not leak into nature. The benefits of being light weight with sufficient mechanical strength, insulation and water repellant properties make plastics an ideal choice still for packaging application. To address the non-biodegradability property of conventional oil-based plastic, a biodegradable type of plastic seems to be the logical approach. Biodegradable plastics can be derived from crude oil such as polyvinyl alcohol and polycaprolactone but the process is quite expensive. Alternatively, a cheaper source can be derived from renewable sources namely: plant, bacteria, and animals. Examples of these are sustainable, eco-efficient and green chemistry renewable sources are chitin from animals, polylactic acid from bacteria and from plant sources include starch, lignin and cellulose. Cereals and tubers are the typical source of starch whereas lignin and cellulose are derived from wood and non-wood forest products.

Abaca plant is an example of non-wood forest products and an indigenous and perennial plant growing luxuriantly in the Philippines. It is an economically important crop that supports more than 200,000 farming families from 56 abaca growing provinces in the country. Scientifically, it is known as *Musa textilis* Nee and is member of the banana or *Musaceae* family. It is primarily cultivated for its fiber which can be extracted from the stalks specifically from the outer covering of the leaf sheath. Abaca fiber has become known worldwide as "Manila Hemp" or simply "Manila". Traditionally, abaca fibers are used as cordage and in handicrafts while processed fibers or abaca pulp are used for paper and specialty paper products. The quality or grade of the fiber is graded based on the its strength, cleanliness, color, texture and length of the

fiber. Moreover, the quality of the fiber determines its uses. sChemically, abaca fiber is composed of cellulose (66.43%), hemicellulose (24.7%), lignin (13.6%), and low water content (0.7%) responsible for its high mechanical strength. These properties make abaca fibers an ideal raw material for nanocellulose production.

Nanocellulose is an emerging nanomaterial that is sustainable, renewable, biodegradable and biocompatible. This material can be used for health and green composites applications such as reinforcement materials for high performance nanocomposites, pharmaceutical, chemical and food additives, optically reflective films, high durability varnishes and bio-plastics. Large scale production of nanocellulose from abaca fiber is an important and initial step in commercializing the technology. The physical, morphological, chemical, thermal, crystallographic, and mechanical properties of extracted nanocellulose can provide valuable information for its various applications mentioned above.

Research works have been conducted on the use of nanocellulose to improve the mechanical strength of packaging materials or bioplastics utilizing starch. In the Philippines, majority of the of starch is produced from cassava. Cassava is a woody shrub of the spurge *Euphorbiaceae* native to South America and is currently cultivated in the Philippines for food, feed, energy and starch. Generally, cassava varieties are distinguished based the hydrocyanide (HCN) content. HCN content that have at least 250mg/kg is categorized as bitter cassava while those with HCN $\leq$ 50mg/kg of cassava are categorized as sweet or edible ones.

2. Production of nanocellulose film from abaca fibers

Nanocellulose has attracted various scientific and industrial communities for economic and environmental reasons with the goal of solving global climate change, resource shortages, and waste disposal. Nanocellulose is essentially biodegradable, renewable, non-toxic, and sustainable carbohydrate-based polymer that can be used as a substitute for oil-based packaging material with comparable mechanical, rheological, and gas barrier properties. Moreover, a large-scale packaging solution require highly transparent, flexible, and inexpensive high performance gas barrier materials. In addition, a low gas permeability as well as mechanical strength and flexibility are important target properties for laminates, coatings, and food packaging films

Generally, cellulose nanocrystals (CNC) and cellulose nanofibrils (CNF) are the two types of nanocellulose that can be produced plant materials. CNC can be obtained using strong acid hydrolysis of cellulose to remove the amorphous region while retaining the crystalline region. On the other hand, CNF

can be produced using chemical, enzymatic, mechanical or combination of various methods. One of the methods used in extracting CNFs is the pretreatment of pulp fiber using 2,2,6,6,-tetramethylpiperidine-1-oxyl radical (TEMPO)-mediated system followed by very mild mechanical disintegration. Saito et al. popularized the method of the oxidation pre-treatment method for hardwood pulp fibers using the TEMPO/NaBr/NaClO system at pH 10. Specifically, the TEMPO has been widely studied for catalytic and selective oxidation of primary hydroxyl groups under aqueous condition that significantly add a negatively charge at the surface that allow the repulsion of individual fibrils.

A 500L capacity locally fabricated nanocellulose extractor has been installed in DOST-FPRDI to provide substantial amount of nanocellulose for production of nanocellulose film. S2 grade abaca fibers purchased from Albay Agro-Industrial Development Incorporation (ALINDECO) were firstly pretreated to using sodium hypochlorite at a pH 2 buffer solution to allow the defibrillation of abaca fibers. Afterwards, the pretreated abaca fibers were subjected to a TEMPO mediated oxidation to extract nanocellulose on a 500 L capacity locally fabricated reactor. A yield of 46.7% white gel material with 2.23% solid content was obtained from an overnight reaction. Transmission electron microscopy scan of the white gel material confirms the production of relatively short highly individualized cellulose nanofibril (CNF) as the diameter of abaca fiber was reduced from 16.28 µm to 3.12 nm with fiber length in the range of 100 nm to 200 nm (Fig. 2-1).

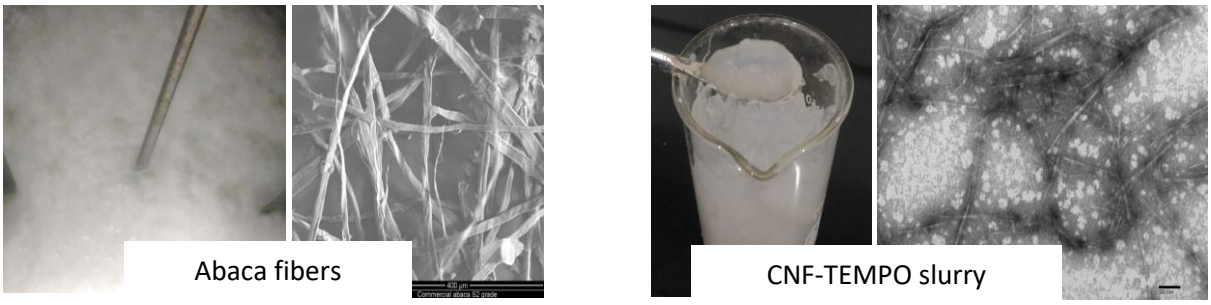


Figure 2-1. TEMPO oxidation of abaca fibers into nanocellulose

Nanocellulose film was prepared using air drying (CNF-VC) and vacuum oven drying (CNF-OD). The effect of CNF concentration on the physical, morphological, thermal and mechanical properties were evaluated. FTIR spectra showed cellulose I spectra between abaca fiber with both the CNF-VC film and CNF-OD film with two distinct peaks at 1620 cm^{-1} and1720 cm^{-1} attributed to the carboxyl group resulting from the TEMPO oxidation. In addition, the carboxyl group decreases in thermal stability of cellulose. Moreover, the XRD scan showed a decrease in crystallinity index of CNF films compared to abaca fibers. CNF-VC film

showed the highest tensile strength at 0.4% concentration with 88.30 MPa, while a 89.72 MPa was observed for CNF-OD film at 0.8% concentration (Fig. 2-2).

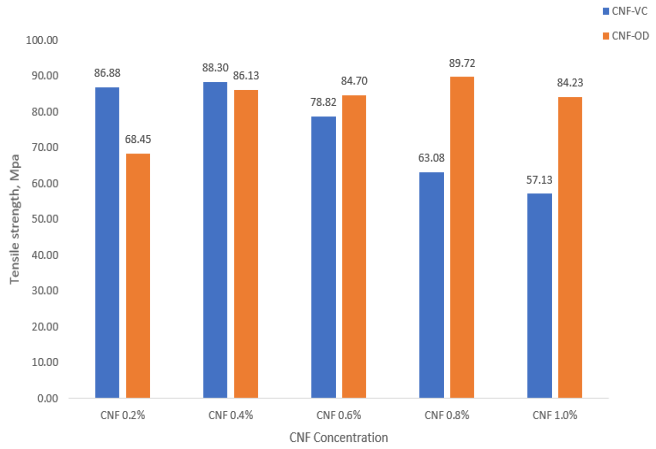
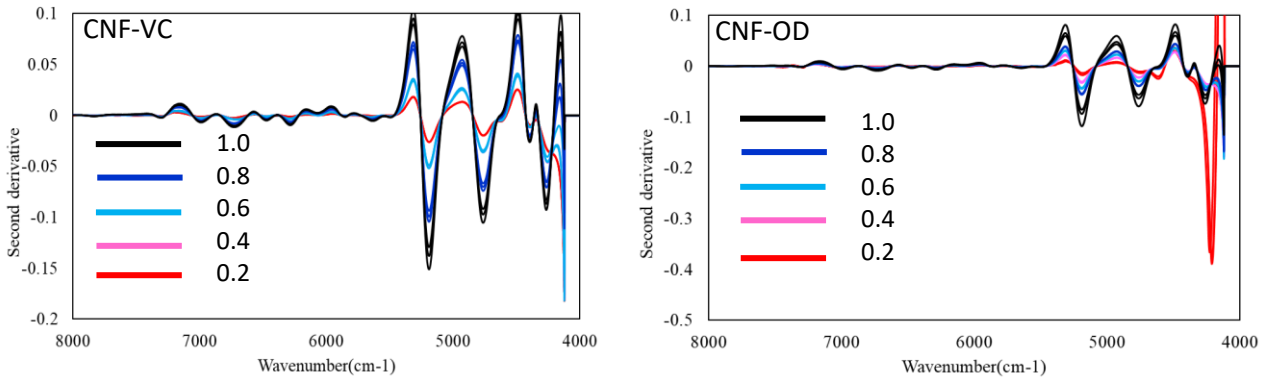


Figure 2-2. Effect of CNF concentration of mechanical properties

3. Characterization of nanocellulose films using spectroscopic analysis

Spectroscopic analysis is a non-destructive method of evaluating samples for their physical, chemical and mechanical properties. Near Infrared (NIR) is an fast and ecofriendly method in predicting the thickness, weight, density and tensile strength of nanocellulose films. NIR spectroscopy is very ideal for organic materials since at 800nm to 2500nm wavelength, the stretching and bending vibration of chemical bonds are clearly visible. The quality and quantity properties of the material can be achieved using the reflected and transmitted light values without going thru special sample pretreatments.

The CNF-VC and CNF-OD films at various concentrations of 0.2%, 0.4%, 0.6%, 0.8% and 1.0% were analyzed using NIR. Five samples were used per replicate for each CNF concentration. Three replicates were prepared for each CNF concentration and a total of seventy-five (75) samples were measured per drying condition. Generally, as the CNF concentration was increase, the NIR spectra showed a higher intensity of absorbance. However, to eliminate the noise, the second derivative of the absorbance is typically plotted.



Partial least square regression (PLSR) showed high correlation for CNF concentration and thickness for both CNF-VC and CNF-OD. However, an acceptable correlation was observed for density and tensile strength. The mechanical property of the film is affected by the single fiber strength and the interfiber bonding. Normally, a high density could correspond to a high tensile strength however only bulk density was calculated which could have not given the true density of the film. In summary, the CNF-VC concentration is highly correlated with the thickness. In addition, tensile strength can be correlated to weight and thickness. Unfortunately, the density could not be correlated amount the other parameters. Lastly, only the CNF-OD concentration and weight showed a high correlation.

4. Application of nanocellulose as reinforcement filler in thermoplastic starch film

Starch is a polysaccharide polymer produced by mostly higher order plants such as cereals and tubers. Chemically, it is a polymeric carbohydrate consisting of amylose and amylopectin with a ratio of amylose/amylopectin that ranges from about 10~20% amylose and 80~90% amylopectin depending on the source and age of the starch and the extraction process used.

Starch can be processed into a plastic commonly referred to as thermoplastic starch (TPS) through gelatinization with the aid of a plasticizer and heat to disrupt the crystal structure thereby allowing the starch to melt and flow freely. Afterwards, upon removal of heat or retrogradation, the amylose and amylopectin recrystallize at a crystal structure normally different from the initial structure. Thermoplastic starch (TPS) is not yet comparable to replace oil-based plastics due to water soluble and moisture sensitivity thereby lowering its low mechanical properties. Several methods have been used such as physical blending, chemical additives, and fiber reinforcement to enhance the property of bioplastic film. Incorporation of cellulose nanofibrils have shown improvement in mechanical and physical properties of thermoplastic starch particularly in tensile strength, water vapor permeability, and oxygen transmission rate. Thus, this study aims to extract starch using local cassava variety as a potential substitute for oil-based plastics, determine its properties and improve its mechanical property using nanocellulose from abaca fibers.

Fresh Lakan I cassava tubers were obtained from University of the Philippines Los Baños – Institute of Plant Breeding (UPLB-IPB). The tubers were washed with water to remove the dirt. Afterwards it was peeled and grated manually and mixed with water in a 1:10 (w/v) ratio. Starch was expressed manually using a muslin cloth and around 3 kilos of white powdery starch was extracted with a 16.66% yield. A globular shaped granules with average diameter of 10.41 um were observed under SEM. Chemically, the starch

contains about 20.96% amylose and 79.04% amylopectin. Based from XRD scans, peaks were observed at around 2θ =15°, 17°, 18°, 20° and 23° characteristic of a Type C structure.

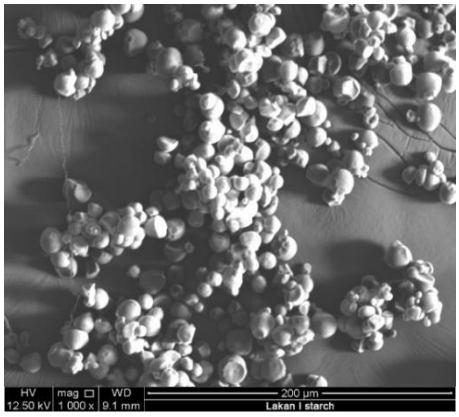
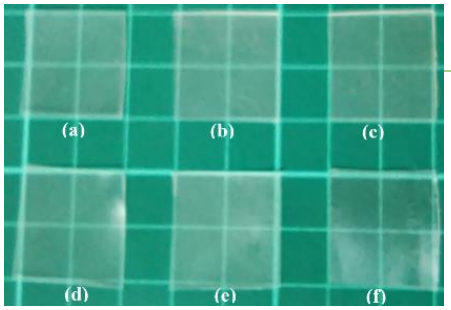


Figure 4-1. Properties of extracted cassava starch

Starch powder were firstly mixed with glycerol and water as plasticizer heated to 80°C for about 10 minutes with continuous mixing. Afterwards, the gelatinized mixture transferred to a mold and air dried under room temperature condition. Physical, morphological, optical, thermal, chemical and mechanical characteristic of the TPS blends were conducted using FESEM, FT-IR, colorimeter, TGA, XRD and UTM.

Thermoplastic starch (TPS) film and its blend with CNF was prepared using vapor casting at room temperature. Subsequently, CNF was added from 0.2% to 1.0% (w/w) of TPS. A semi-transparent flexible whitish film was formed (Fig. 4-2). However, colorimeter values correspond to a bluish color.



TPS blends	L	a	b
Neat TPS-0%CNF	88.91	4.16	-10.02
0.2% CNF	88.52	3.58	-9.83
0.4% CNF	89.63	3.73	-9.93
0.6% CNF	88.54	3.41	-9.12
0.8% CNF	88.56	3.57	-8.94
1.0% CNF	89.02	3.44	-9.42

FTIR scan showed the characteristic pattern of starch with little effect from CNF. Thermal stability of the TPS film slightly decrease from the addition of CNF. XRD spectra reveal the transformation in crystallinity of starch into TPS. Moreover, the addition of CNF in the TPS matrix was evident in the higher peak intensity and 2Θ=18° and 22.6° corresponding to the amorphous and crystalline region of cellulose. Lastly, the mechanical property of TPS film generally increased upon the addition of CNF. A maximum tensile strength was observed from neat TPS to 0.6% CNF concentration with 5.73MPa to 15.1MPa respectively.

General Conclusion

The extraction of nanocellulose using TEMPO oxidation of abaca fiber at a bench scale production is an initial step towards its commercialization. A conversion yield of 46.67% was obtained using high chlorite content and reacted for at least 24 hours. A highly hygroscopic whitish gel like material with solid content of 2.23% characteristic of nanocellulose material. Moreover, TEM reveals the high individualized CNF with 3.12nm in diameter and over 100nm to 200nm in fiber length. FTIR also confirms the effectiveness of carboxylation of cellulose using TEMPO as evident to peak associate with it. The extraction process did not affect the cellulose structure but slightly reduced its thermal properties. Increasing the CNF concentration generally increased the mechanical property of CNF films. However, increasing the CNF concentration might lead to fiber agglomeration which affect the fiber to matrix bonding that would generally reduce the mechanical property of CNF films. CNF is an ideal candidate to reinforce TPS starch due to its biocompatibility and chemical structure. Extraction of starch using wet extraction from Lakan I variety yielded 16.67%. Physical, chemical, crystallographic and morphological characteristic of extracted starch is within the reported characteristic of a typical cassava starch. The use of water and glycerol as plasticizer and heated at 80°C with constant stirring enable the complete gelatinization of the mixture. Acetic acid also provided the antimicrobial growth of the synthesized TPS films. A whitish translucent film was visually observed. However, colorimeter values correspond to a bluish color. In addition, a homogenous matrix was evident from the SEM scans. The effect of reinforcing TPS using CNF could not be distinctively seen from the FTIR analysis due to the similarity in chemical structure of starch and cellulose. However, XRD scans indicates the presence of cellulose as evident to the increase peaks at 2Θ=18° and 22.6° corresponding to the amorphous and crystalline region. similar patterns after reinforcement with CNF probably due to the low loading of CNF into the matrix. However, thermal analysis showed the slight decrease on the onset temperature and the Tmax of TPS film. Lastly, the application of CNF as reinforcement filler in thermoplastic starch film increase the mechanical property of TPS film.

Activities during PhD course

1. Dr. Tsuguyuki Saito laboratory visit, Department of Biomaterial Sciences, University of Tokyo. January 21, 2020
2. Laboratory orientation at system engineering for biology, January 2020
3. Laboratory visit at Forest Chemistry with Profs. Matsusihta and Aoki and at Wood Physics laboratory with Prof. Yamamoto. January 2020

Publications

1. Production of nanocellulose film from abaca fibers. Crystals 2022, 12, 601. https://doi.org/10.3390/cryst12050601
2. Characterization of nanocellulose film using spectroscopic analysis (In preparation)
3. Application of nanocellulose as reinforcement filler in thermoplastic starch film (In preparation)