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主　論　文　の　要　旨

論文題目　Production of Novel Cellulosic Materials from Tropical Plants

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論　文　内　容　の　要　旨

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. Replacement of non-biodegradable plastic with biodegradable plastics seems the logical approach to reduce the environmental effect of plastics. 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, *Musa textilis* Nee, is member of the banana or *Musaceae* family which is an indigenous and perennial plant growing luxuriantly in the Philippines. It is primarily cultivated for its fiber which can be extracted from the stalks specifically from the outer covering of the leaf sheath. Chemically, 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 innovative bio-plastics. The extraction of nanocellulose from abaca would provide the initial step for sustainable local production. Moreover, its application as a bioplastic and as reinforcement filler in starch bioplastic could be a potential substitute for non-biodegradable oil-based packaging films.

Chapter 2 entitled "Production of nanocellulose film from abaca fiber" uses a 500L capacity locally fabricated nanocellulose reactor. Commercial bleached abaca fiber was chemically treated using 2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) to liberal the nanocellulose. A white gel material was obtained after at least 24 hours of reaction with 2.23% solid content. Transmission electron microscopy (TEM) showed cellulose nanofibrils (CNF) having an average fiber diameter of 3.12nm and fiber length in the range of 100-200nm. The nanocellulose was then transformed into a transparent bioplastic film at various CNF concentration with 0.2%, 0.4%, 0.6%, 0.8% and 1.0% and dried under room temperature condition (CNF-VC) and vacuum oven condition (CNF-OD). Scanning electron microscopy (SEM) reveal the transition of a smooth surface into a rough surface as the CNF concentration was increased. Fourier transform infrared spectroscopy (FTIR) showed attached carboxylate group evidently at peak 1720 cm^{-1} for both CNF-VC and CNF-OD. Xray diffraction (XRD) scans of abaca fiber and CNF films showed similar diffraction pattern with 2θ = 18° (101) and 22.6° (002) confirming the retaining of the original cellulose I structure after the TEMPO oxidation. The maximum tensile strength was at 0.4% CNF-VC and 0.8% CNF-OD with 88.30MPa and 89.72MPa respectively.

Chapter 3 entitled "Characterization of nanocellulose films using spectroscopic analysis" focuses on using near-infrared (NIR) to predict the physical and mechanical properties from using known set of data from CNF-VC and CNF-OD films. The CNF-VC and CNF-OD films prepared at various concentrations of 0.2%, 0.4%, 0.6%, 0.8% and 1.0% were analyzed using NIR. Generally, as the CNF concentration was increase, the NIR spectra showed a higher intensity of absorbance. Partial least square regression (PLSR) showed high correlation for CNF concentration and thickness for both CNF-VC and CNF-OD. However, unacceptable correlation was observed for density and tensile strength. 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.

Chapter 4 entitled “Application of nanocellulose as reinforcement filler in thermoplastic starch film” focuses mainly on improving the mechanical strength of thermoplastic starch film from a local source of starch. The starch was extracted from Lakan I cassava variety with a yield of around 16.67%. SEM micrographs reveal a globular shape with average diameter of 10.41um. XRD scans showed peaks at around 2θ = 15°, 17°, 18°, 20° and 23° characteristic of a type C structure. Furthermore, the chemical analysis of starch having a 20.96% amylose and 79.04% amylopectin ratio confirming chemical characteristic of cassava starch.

Cassava starch was gelatinized using water and glycerol and acetic acid as plasticizers and heated at around 80°C with constant stirring to allow starch gelatinization into thermoplastic starch (TPS) and to be molded in a desired shape. Various concentration of CNF (0.2%, 0.4%, 0.6%, 0.8% and 1.0%) was added to the starch mixture to determine the effect on the mechanical strength of the TPS film. A gelatinized starch mixture reinforced with CNF was allowed to retrogradation under room temperature condition.

A semi-transparent whitish film was observed after drying. However, colorimetric average value of L*, a*, and b* around 88.85, 3.55, and -9.45 corresponds to a bluish in color. FTIR spectrum showed no significant difference between neat TPS and TPS blends due to similarity between the chemical structure of starch and cellulose. However, thermal analysis using TGA showed the effect of CNF on the TPS film. A slight decrease in the degradation temperature (1.82%) and onset temperature (5.98%) was observed.

The effect of incorporating CNF on the crystallographic property of TPS was evaluated. XRD scans showed similar peaks at 2θ = 17°, 20°, and 21.6° with no clear evidence about the incorporation of CNF probably due to the small amount of that was added. XRD scan of TPS film showed a more amorphous type of material with wider and lower peaks compared to semi-crystalline starch powder. Surface morphology of the TPS films showed a generally homogenous matrix upon the addition of CNF. Tensile strength of the TPS generally increased as CNF was incorporated into the matrix. The maximum tensile strength was observed at 0.6% CNF concentration with 15.1MPa. An increased of 153.63% resulted from the incorporation of CNF to neat TPS film having an initial tensile strength of 5.73MPa. The application of CNF as reinforcement filler in TPS film showed the potential use as a replacement in oil-based plastic.