Synthesis of Cellulose Nanofiber from Cogon Grass (*Imperata cylindrica*) for Bioplastic Production

Mary Novel S. Abkilan[1], Lourel Nicole B. Atilano[1], Araezza Ella G. Monton[1], Lovely Charmaine R. Gomez[2], and Ashraf R. Khater[1]

[1] College of Engineering, University of Negros Occidental-Recoletos, Incorporated, Bacolod City, Philippines
[2] Asian Alcohol Corporation, Pulupandan, Negros Occidental, Philippines

ABSTRACT

The dependence and reliance on lightweight materials, generally plastics, for many applications has resulted in global plastic pollution and consequent environmental effects. The situation of marine garbage pollution in the Philippines is critical and concerning. Manila Bay and Pasig River, two common bodies of water in the country, are reported to be extensively polluted by plastics. With this problem, the researchers conducted a study to address the issue of water pollution caused by discarded plastics in the Philippines by utilizing cellulose nanofiber (CNF) extracted from cogon grass and reinforced with polyamide-6 (PA6) to improve the characteristics, especially biodegradability, of plastics. A percentage ratio of 60:40, 70:30, and 80:20 was used for the mixture of CNF and PA6, and outstanding tensile characteristics were found. Based on their tensile strength performed using PASCO – Wireless Force Acceleration, Sample 2 (70:30) exhibits better tensile strength than Sample 1 (60:40). Meanwhile, a T-test for independent samples was used to determine the significant difference in the tensile strength between the samples of bioplastic and commercial plastic. Results showed that Sample 2 has a higher tensile strength than Plastics. Additionally, samples 1 and 2 had a rate of weight loss of 14.81% compared to the 0% weight loss of commercial plastic within seven days. The significant difference in weight reduction between trials was determined using a one-way analysis of variance (ANOVA). There was no significant difference in the weight loss between the samples. It shows that both models have the same biodegradability.

Keywords
cellulose nanofiber; polyamide-6; acid hydrolysis; ultrasonication, bioplastic, tensile strength, plastic, Philippines, pollution

INTRODUCTION

The dependence and reliance of man on lightweight materials, generally plastics, for so many applications had resulted in global plastic pollution and consequent environmental effects. According to the meta-analysis of Greyer et al. (2017), various kinds of plastics were identified. These include 23% polyethylene or PE, 20% polyesters/polyamide, 13% polypropylene or PP, and 4% polystyrene or PS accounted for 74% of global plastic production in 2015. Plastics, being non-biodegradable, could live for hundreds of years, and some may be swept away by ocean currents and even reach arctic regions. These plastics may contain exotic species that could jeopardize the marine ecosystem's stability and endanger human health (Rochman et al., 2015). Manila Bay, a catch basin for the Philippines' contributing riverine systems, is reported to be extensively polluted by plastics. Meanwhile, in the Pasig River alone, $3.21x10^4$ MT of plastics were donated to the embayment each year, making it one of the most polluting point sources on Luzon's west coast (Abreo 2018).

Cellulose $(C_6H_{10}O_5)_n$ is a polysaccharide composed of covalently bound b-D-glucopyranose units. Their origin and extraction procedure determine natural cellulose structures' shape, length, and diameter. Converting easily accessible cellulose into nano-cellulosic forms or combining it with appropriate polymers is crucial for improved composites (Menon et al., 2017). Cellulose nanoparticles produced from the fibers are currently essential products for almost every aspect of the endeavor of humankind. CNP has been discovered to have the qualities needed to replace several commonly used types of equipment like glassware, cement, alloys, fabricated polymers, and textiles. CNPs have primary benefits, including that they are derived from organic, renewable resources, are ecologically friendly, cost-effective, and biodegradable (Agwuncha et al., 2019).

Cogon grass has been rated one of the ten leading worst weeds on the planet because of its propensity to invade, spread, compete with, and disrupt ecosystems and is considered a dangerous pest in tropical and subtropical locations worldwide (Jumaidin et al., 2020). Cellulose is a polysaccharide composed of covalently bonded b-D-glucopyranose units. Accessible cellulose can be converted into nano-cellulosic forms by combining it with appropriate polymers is crucial for improved composites (Menon et al., 2017). The thermo-mechanical properties of composites were improved by polyamides, polymeric reinforcing material, and Nanocellulose reinforcements. Polyamide-6 is the prevalent polyamide (PA6, also called nylon-6). Because of its availability and high mechanical properties, this flexible, renewable, and nanostructured polymer is a popular choice. A compatibilizer compounding surface interactivity may be obtained without reinforcement because of PA6's and CNF's hydrophilicity (Sridhara et al., 2021).

Chemical and mechanical procedures can be used to extract cellulose from plant fibers utilizing alkalization, bleaching, and acid hydrolysis techniques, and they can be extracted in nano and microforms (Ranganagowda et al., 2019). When nanocellulose is properly distributed, it has a higher specific surface area, which aids interface adherence to the polymeric matrix. It's also feasible to chemically alter its surface to change its characteristics, which is useful in applications like foams and adhesives (Sridhara et al., 2021). This study considers the extraction of cellulose nanofiber from Imperata Cylindrica (cogon grass) to produce bioplastics. Nichols (2021) defined extraction as when a compound(s) transference from a solid or liquid phase to a different solvent or phase. The most typical method in a chemistry lab is liquid-liquid extraction. The most common design is to have one aqueous layer and one organic solvent layer. When components move from one layer to the next, they are "extracted."

According to Kafy et al. (2017), CNF has high-level mechanical properties. However, it is concise to be used for firm and eco-friendly fibers, for example, CNF for reinforced compounds. The following are measures used to strengthen the material regarding tensile stress. A study made by Savadekar and Mhaske (2012), the study proved that the addition of Nanocellulose fibers is one component that boosts the film's tensile strength. According to Daelemans (2015), the influence of the solution parameters on the steady-state behavior during electrospinning and the resultant fiber morphology is studied using scanning electron microscopy and differential scanning calorimetry in order to trace and understand the dominant parameters that allow for the desired reproducible characteristics. According to the findings, the amount of acetic acid added to the solvent formic acid substantially affects the steady-state behavior and fiber morphology. For testing Tensile Strength, Michigan Technological University (2022) stated that the basic principle behind a tensile test is to clamp a material sample sandwiched between two fixtures known as "grips." The material's dimensions, such as length and cross-sectional area, are known. The weight will be applied to the material gripped at one end while the other is fixed. The weight will keep increasing (also known as the load or force) while measuring the change in length of the sample. The outcome of this test is a graph of load (weight) vs. displacement (the amount it stretched). In a study made by Kasmuri and Zait (2018), to measure the tensile strength, they developed a simple laboratory replica of a typical complex tensile machine, Instron's Tensile Testers, described in the experiment on the strength test. Attached to and hung from a laboratory clamp is a plastic substance with defined dimensions (width and thickness first, length second). Attached to the bottom of the specimen is a bucket with a handle used to store exact weights. A specified load is applied as individual weights are put into the bucket, translated to stress (force/unit area) using the sample's known cross-sectional area. Strain is measured by measuring the sample's initial length and incrementally increasing it with each additional load. After adding weights and measuring each new length, all the necessary information may be presented.

The main problem with plastic is that a significant amount of it is utilized to construct disposable packaging or other short-lived products that are permanently discarded within a year of creation. (Haward, 2018). To reduce this situation, the study by Sridhara et al. (2021) suggested using cellulose nanofiber (CNF) as a bio-based reinforcement in engineering polymer composites. Through solvent casting, the study created a long-term method for reinforcing polyamide-6 with CNFs. The approach provides an energy-efficient route to well-distributed PA6 bio-composites with high CNF content.

Generally, the study aims to produce environmentally friendly plastics where the cellulose can be extracted from the natural plant *Imperata cylindrica* (cogon grass) and reinforced with polyamide-6 to improve the characteristics, especially biodegradability, of plastics which will help reduce plastic pollution. Specifically, the study aims to know the percentage yield in terms of mass content of cellulose nanofiber extracted from Imperata cylindrica or cogon grass as a raw material under acid hydrolysis conditions, to know the ratios of the amount of cellulose nanofiber extraction and polyamide-6 in terms of its volume that could strengthen the tensile strength in MPa of the sample, to know the significant difference in terms of the product's tensile strength (MPa) compared to the commercial one, lastly, to know the change in mass of the selected ratio of CNF-PA6 mixture when it is soaked in seawater for seven days.

During bio-plastic production, the researchers conducted the extraction of cogon grass and other experiments at the University of Negros Occidental-Recoletos Chemical Engineering laboratory. The materials used came from different sources. Polyamide-6 pellets were bought from an online store, and cogon grass was manually harvested. Other reagents used were available from the said laboratory. The test used during product testing was only limited to tensile strength test and biodegradability test. Due to the unavailability of a tensile testing machine for plastics in Negros, the equipment used for testing the tensile strength of bioplastic was PASCO – Wireless Force Acceleration, available in the University of Negros Occidental - Recoletos Senior High School Laboratory. While on the biodegradability test, the number of days in determining the degradation of the samples is limited only to seven days due to time constraints. The plastic bag used for comparison is an ordinary plastic bag found in commercials. A comparative test was made for tensile strength and biodegradability to assess the significant difference between the commercial plastic bag and experimented products.

This research study will benefit the fisherfolk because they are the ones who usually utilize the ocean in fishing. A clean and pollution-free ocean can minimize the problems in propeller entanglements and damage to fishing gears. This research is also beneficial to potential investors, who can benefit from the study because the government offers incentives to persons who invest in plants that provide cellulose. The research will also be helpful in the environment, specifically the marine ecosystem, because it is leaning toward decreasing the cases of water pollution in the ocean. This study may enable the government to be aware of other benefits acquired from cogon grass that may be considered in relevant programs and plans for the welfare of its stakeholders. This research can also help chemical engineering students understand how to extract cellulose nanofibers and use them as an additive in producing bioplastics. Lastly, this study may use this study as a basis for further studies about cellulose nanofibers from cogon grass as an additive in bioplastics. Moreover, through this study, future researchers can also consider investigating other enhancements that can improve the mechanical properties and tensile strength of bioplastics.

METHODOLOGY

The study used an experimental approach to obtaining data. To sustain the study, the researchers seek different processes and strategies to utilize the cogon grass that is widely spreading across the country. The study by Mohd Kassim et al. (2015) shows that cogon grass consists of 36.6% cellulose; by this information, cogon grass can be a source of fiber that can reinforce strength in polymers such as polyamide 6.

The researchers gathered knowledge about bioplastic production safety measures, instrumentation, and design standards by reading various linked literature from journals to books and other sources.

For the primary process of extracting cellulose nanofiber from cogon grass, the raw material had undergone several procedures like Alkaline treatment, Bleaching, and Acid hydrolysis. Polyamide-6 was dissolved using a glacial acetic acid. The extracted CNF was then mixed with the dissolved Polyamide-6, dried, and cast into bioplastics. The researchers used articles and literature with chemical engineering textbooks and handbooks to design the process and materials to be used in the collection of data.

The researchers used the gathered data from the study of Shridhara et al. (2021) and Jumaidin et al. (2020) as a guide in creating a series of procedures. The first significant procedure was to extract the CNF from the raw material, which is the cogon grass. For the alkaline treatment, it was done to remove the lignin and hemicellulose from the cogon grass to increase the density of the fiber. In this treatment, the raw material was treated using 4% NaOH solution under constant stirring on a hot plate.

The next step, Bleaching, was done to remove unwanted intrinsic coloring components from the textile material. This process also helps in removing residual lignin that was not removed from the previous treatment. The researchers used the mixture of 5% NaOH and H_2O_2 using the 1:1 ratio in bleaching the pre-treated fibers at 50 degrees Celsius under constant stirring for 1 hour. The suspension was then filtered and washed using distilled water. The fibers were then dried at 80 degrees Celsius in an incubator for 4 hours (Sridhara, 2021).

For the isolation of cellulose nanofibers, acid hydrolysis was performed using a 9.15 M H_2SO_4 solution and, with the guidance of the Taguchi approach, a statistical strategy for analyzing many variables without an excessive amount of experimentation. After acid hydrolysis, the resulting suspension was centrifuged and then ultrasonicated to thoroughly mix the polymers.

The 2nd major procedure consists of Polyamide-6 breakdown, mixing, and cutting the CNF-PA6 sample. To mix the PA6 with the CNF, the researchers used the acetic acid solvent to break down the PA6. After breaking down the Polyamide-6, it was mixed with a different amount of CNF (60%, 70%, 80%), dried, cast, and tested according to their tensile strength and biodegradability.

For the tensile strength test, due to the unavailability of ASTM D638, a UTM for tensile strength test for plastics, the researchers used the PASCO – Wireless Force Acceleration to obtain the elongation and force at the break of the sample. With the received data from the PASCO – Wireless Force Acceleration, the researchers used the Young's Modulus of Elasticity formula below:

For the biodegradability Test, the samples were submerged in the seawater collected by the researchers and were observed for seven days. The data gathered were used to solve the % weight loss of the samples and the commercial one.

The researchers established the resulting data according to the different pieces of study that they had read and from the laboratory experiment they had conducted.

This study was limited to making bioplastics from the admixture of CNF to PA6. Other products from the CNF-PA6 mixture were not included. These tests only included tensile strength and biodegradability tests, other tests, such as the morphological tests, were not included.

RESULTS, DISCUSSION, AND IMPLICATIONS

The percentage yield obtained from a mass of 54.9 grams of cogon grass was 18.76% under acid hydrolysis conditions. The value of the CNF yield is within the range of the reported literature for nanocellulose obtained under sulfuric acid hydrolysis which varies from 7.8 % to 27.6 % (de Carvalho Benini et al., 2018). Moreover, given the sulfuric acid concentration of 60 % by weight, the reaction time of 30 minutes, the pulp-to-solution ratio (g/mL) of 1:20, a temperature of 60 degrees Celsius, initial mass of cogon grass in fibers (in grams) to be 54.9 g, and the mass of treated cellulose nanofiber (CNF) in grams to be 10.298 g, the percent yield of CNF was calculated to be 18.76%.

The different ratios of CNF and PA6 mixture were used to determine the ratio of the amount of cellulose nanofiber extraction and polyamide-6 in terms of its volume that could strengthen the tensile strength in MPa of the sample. A volume of 6 mL and 7 mL of CNF was used in sample 1 and sample 2 respectively. While 4 mL and 3 mL of PA6 was used in sample 1 and sample 2 respectively.

For the tensile strength test of sample 1, three trials were conducted. In trial 1, the tensile strength obtained is 0.0135 MPa, in trial 2, 0.0128 MPa, and in trial 3, the tensile strength of the mixture is 0.0132. The mean of the tensile strength test trials in Sample 1 is 0.0132 MPa.

Three trials were also conducted for sample 2. In trial 1, the tensile strength obtained is 0.01442 MPa, in trial 2, 0.01388 MPa, and in trial 3, the tensile strength of the mixture is 0.014. For the mean of the three trials, the obtained value is 0.0141 MPa. It is noted that, Sample 2, which has a 70%:30% CNF - PA6 mixture ratio, has better tensile strength than Sample 1, which has a 60%:40% CNF- PA6 mixture.

The tensile strength of Sample 2 after computing the Young's Modulus (MPa) equation at trial 1 was found out to be 0.01442 (MPa), trial 2 has the value of 0.01388 (MPa), and at trial 3, the value is 0.014 (MPa). The 70%:30% ratio of CNF - PA6 mixture and at trial 1 has the highest tensile strength compared to the other two trials. The measured tensile strength of Plastic Sample after computing the Young's Modulus (MPa) equation at trial 1 is found to be 0.00475 (MPa), trial 2 has the value of 0.00425 (MPa), and at trial 3, the value is 0.00475 (MPa) same as trial 1.

The bioplastic sample shows a higher tensile strength, especially trial 3, which has a tensile strength of 0.01442 (MPa). In contrast, the plastic sample has the same value of 0.00475 (MPa) in trial 1 and trial 3 but is still lower compared to sample 2 of bioplastic.

A T-test independent sample was used to determine the significant difference in the tensile strength between treatments. The difference was significant in the tensile strength between treatments $p = 0.000^*$. It shows that Sample 2 has a higher tensile strength than Plastics.

The biodegradability test of the sample 1 and sample 2 of bioplastic and commercial plastic was determined after seven days. This test carried the result of bioplastic and commercial plastic mass reduction in a 100 mL sample of seawater. The initial mass of all trials of the three samples, including the commercial plastic, was 0.027 grams on day 1. On day 3, the average mass of sample 1 and sample 2 was reduced to 0.026 grams and 0.025 grams, respectively, with a rate of weight loss of 3.7 % and 7.41 %, respectively, while the mass of the sample of commercial plastic was still the same. Lastly, on day 7, both sample 1 and 2 reduced their mass to an average of 0.023 grams with a rate of weight loss of 14.81 %, while the mass of the sample of commercial plastic was still the same. The formula for percentage weight loss was based on the study of Kasmuri et al. (2018). Therefore, the value of 14.81% is the optimum rate of weight loss for both samples, which indicated that the bioplastic had a good ability to biodegrade compared to the commercial plastic when soaked in seawater within seven days. Hence, the obtained result is within the period of biodegradability of the recent study by Folino et al. (2020) that bioplastics can degrade in seawater within ninety days.

There was no significant difference in the biodegradability test between treatments [$F(2, 3) = 2.385$, $p = 0.240$]. It shows that both treatments have the same biodegradability. One-way Analysis of Variance (ANOVA) was used to determine the significant difference in the weight loss between trials. There was no significant difference in the weight loss between the samples [$F(2, 3) = 2.384$, $p = 0.240$]. It shows that both samples have the same biodegradability.

Imperata cylindrica is widespread and known as an invasive plant. Despite this, the results show that it can be a promising source of cellulose nanofiber and analogous to other plants that can yield cellulose nanofibers. Moreover, it can be utilized as a natural source for industrial uses, such as reinforcement for composite materials. Based on the outcomes, it can be implied that cogon grass can be a natural source of producing bioplastics and can be similar to starch-based bioplastics. Sample 2 of bioplastic has higher tensile strength and has faster degradation than sample 1 compared to commercial plastic. Thus, this implies that the volume of cellulose nanofiber should be higher to improve the tensile strength and speed up bioplastic degradation. However, a much higher volume of CNF is not recommended as sample 3 did not solidify. As a result, the ratio of the amounts of CNF and PA6 should not be far from each other to justify the compatibility of Cellulose Nanofiber and Polyamide-6. This research also discovers that an alternative to Formic acid is the Glacial acetic acid. The pungent odor of the acid wasn't removed; thus, the smell of vinegar still lingers, but the researchers were still open to the possibilities of using glacial acetic acid to make bioplastic. More importantly, it can address the widespread problem of marine plastic pollution. Visible impacts of the said issue could lessen, such as ingestion and suffocation of marine species.

As commercial plastics continue to pollute our waters, bioplastics became the first counters to minimize the outbreak of marine pollution. Bioplastics can degrade within the environment, but conditions are needed to achieve faster degradation. This research focuses on marine pollution and can be a basis to help chemical engineers produce a product that uses cellulose nanofibers of cogon grass to improve the biodegradability and tensile strength of bioplastic.

Based on the results of this study, bioplastics are sustainable, largely biodegradable, and biocompatible. According to Ashter (2016), bioplastics are plant-based products. Therefore the consumption of petroleum for the production of plastic is expected to decrease by 15–20% by 2025. As part of a developing circular economy through plant design, the rapid accumulation of plastic waste is driving international demand for renewable polymers with better attributes, like complete biodegradability to CO_2 without toxic byproducts. The diversity of bio-based feedstocks opens up the opportunity to produce an expanding range of renewable plastics. Biodegradable polymers should, in theory, dissolve entirely in CO_2 and water, leaving no hazardous outcomes.

CONCLUSION AND RECOMMENDATIONS

One of the main reasons for the study is to address the problem of plastic pollution in the ocean, which has already reached dangerous levels. Manufacturing plant-based plastics is one of the many answers to this challenge. Consumers and manufacturers are pushing for an alternative to the ubiquitous material. More study on the impact of consuming so much plastic emerges, and bioplastics have emerged as a potential option. These bioplastics not only help with breaking down and biodegradability, but they also generate far fewer greenhouse gases than traditional plastics over their lifetime. If they end up in marine habitats, they'll break down into micro-sized fragments, last for decades, and threaten marine life, just like petroleum-based plastic.

Because of its propensity to invade, spread, compete with and disturb ecosystems, cogon grass has been named one of the top 10 worst weeds. This rhizomatous perennial plant has long been regarded as a harmful pest in tropical and subtropical areas worldwide. As a result, the researchers concluded that cogon grass is one of the plants that can provide cellulose nanofiber. Making bioplastics from cogon grass was designed to be cost-effective, efficient, and profitable. For the Biodegradability Test, it is recommended in this test to submerge the product in seawater for 90 days to determine the complete degradation of bioplastic in the marine environment.

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