

Starch Based Bioplastics Reinforced with Cellulose Nanocrystals from Agricultural Residues

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Abstract—Cellulose nanocrystals (CNCs) from garlic stalks and rice straws, two common agricultural residues in the Philippines, were isolated and used to reinforce starch-based biocomposite films. The isolated CNCs from garlic stalks are spherical and have an average diameter of 35 nm and crystallinity of 62%. On the other hand, short, rod-like CNCs with particle diameter ranging from 10-12 nm and crystallinity index of 76% were isolated from rice straws. Starch-based biocomposite films with varying amount of the isolated CNCs as reinforcing filler were prepared by solution casting and evaporation method. Mechanical test revealed that both tensile strength and Modulus increased with the addition of CNC. Finally, CNC-reinforced films had lower moisture uptake than non-reinforced films.

Keywords—Garlic stalk, rice straw, cellulose nanocrystals, bioplastics, mechanical properties.

I. INTRODUCTION

REINFORCEMENT of bio-based materials has been an important concern among material scientists in the past decade evident from numerous reports about reinforced bioplastics. Great attention has been given towards the improvement in mechanical properties of bioplastics because they cannot completely surpass the wide applications of petroleum-based plastics in the market despite the problems posed by the latter to the environment. Thus, reinforcement is needed to bridge the gap between bio-based and petroleum-based plastics.

One technique to reinforce a material is through the incorporation of fillers. Some of the common reinforcing fillers are clay, talc, silica, glass fiber, carbon black, and fibers derived from biomass [1]. Cellulose is the most abundant biomass present as fiber bundles in the cell walls of plants or produced

by some bacteria and marine organisms. If the fiber bundle is deconstructed to nanoscale dimension, the nanofibrils show remarkable mechanical properties and are a good candidate as reinforcing material. Within these fibrils are the crystalline and amorphous regions of cellulose. Crystalline cellulose is much stronger and stiffer, and considered to be a better reinforcing agent than amorphous cellulose or the native cellulose itself [2]. This concept has gained a lot of interest among researchers worldwide evident from numerous reports on the isolation and application of crystalline cellulose on composite material and the major sources of CNCs were woody plants, cotton, potato peel wastes, sugarcane bagasse, bamboo, coconut husks etc [3].

Cellulose from different sources exhibits a wide range of crystallinity, moisture content, surface area, porous structure, and molecular weight. It is expected then that CNCs from other sources will also show different properties. Moreover, the crystalline cellulose is isolated in the form of nanocrystals, often by acid hydrolysis and the extent of hydrolysis, the type of acid used, and other mechanical treatments employed during isolation can also affect the size and crystallinity of CNCs. From this point of view, our group has reported on the isolation of CNCs from rice straw and garlic stalks, two of the common and abundant agricultural residues in the Philippines. The reinforcing effect of CNC in starch-based bioplastic was also investigated. Results of this study could provide a novel application for garlic stalks and rice straws and could also address the pressing environmental issues on non-biodegradable and petroleum-based plastics.

II. EXPERIMENTAL

A. Materials

Rice straws (R216 variety) and garlic stalks were collected from a farm in Science City of Muñoz and San Jose City, respectively in the Philippines. Sodium hydroxide and sodium hypochlorite for the initial pulping process were of technical grade and purchased from Alyson's Chemical Enterprise. Reagent grade sulfuric acid, glycerol and acetic acid were obtained from Ajax Chemicals. Food grade corn starch was used for biocomposite preparation.

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B. Isolation of cellulose nanocrystals

The isolation of cellulose nanocrystals from garlic stalks and rice straw followed the procedure reported in literature [4] with minor modification. The isolation involved two major steps: the alkali treatment and acid hydrolysis. Due to difference in the nature of each sample, different conditions as shown in Table 1 were employed for each sample.

TABLE I
ALKALI AND ACID TREATMENT CONDITIONS FOR GARLIC STALK
AND RICE STRAW

Sample	Alkali treatments	Acid hydrolysis
Garlic Stalks	15% w/v NaOH at 60°C for 4 hrs.	50% v/v H ₂ SO ₄ at 35°C for 5 hrs.
Rice straw	10% w/v NaOH at 60°C for 2 hrs	50% v/v H ₂ SO ₄ at 35°C for 3 hrs.

The procedure is described briefly: Fifty grams sample were transferred into a two-liter beaker and alkali treated to remove lignin and other pectic substances. The insoluble fibers were then bleached using 1% v/v sodium hypochlorite solution buffered to a pH of 5 by an acetate buffer. The bleached fibers were then washed repeatedly with water until the washing becomes neutral and then air dried. Ten grams of the bleached fibers were acid hydrolyzed according to the condition shown in the table. Hydrolysis was stopped by the addition of cold distilled water. The mixture was then centrifugated at 10,000 rpm for 10 minutes to coagulate the crystals and remove the excess sulfuric acid. The coagulated CNC was then suspended again in water and dialyzed using a dialysis membrane with a molecular weight cut off of 12kDa (Spectrapor4) to further remove the excess acid. The resulting suspension after the dialysis was then sonicated for 10 minutes. The collected suspension was stored in a refrigerator and a portion of it was freeze dried for analyses that required dry samples. The percentage of CNC in the suspension was determined using gravimetric method.

C. Characterization of the isolated CNC

Crystallinity was investigated using a X-ray diffraction instrument at ambient temperature by step scanning at a target voltage of 40 kV and current of 40μA. Crystallinity of samples before and after each chemical treatment was also determined. The crystallinity index (CI) was computed using the equation developed by Segal and coworkers [5].

$$CI = \frac{I_{002} - I_{\text{Amorph}}}{I_{002}} \times 100$$

Where, I_{002} is the maximum intensity that corresponds to the crystalline phase and I_{Amorph} is the minimum intensity that lies between the two most well defined peaks and corresponds to the amorphous phase.

Transmission electron microscope was used to determine the shape and size of the isolated cellulose nanocrystals. Five milligrams of the suspension was diluted to 50 mL with methanol. A 5-mL aliquot of this suspension was further diluted

five-fold. A drop of suspension was placed onto carbon-coated grid then dried at room temperature. This was then examined using TEM model JEOL JEM 1010 operating at 100kV. The average diameter of the CNC was measured using SEM afore.

D. Starch-CNC biocomposite film preparation

Films were prepared by solution casting and evaporation process using corn starch as the polymer matrix. Ten grams of corn starch was suspended in distilled water (200 ml) and heated at 60°C for 15 minutes for gelatinization. Suspension of cellulose nanocrystal was slowly added to the starch solution. The amount of CNC was varied to produce starch to CNC ratios of 100:2.5 (T1), 100:5 (T2), 100:10 (T3) and 100:15 (T4) based on dry weight. Glycerol (3g), as a plasticizer, was then added and the mixture was stirred for two hours at a temperature of 80°C. The mixture was cooled and cast on glass plates and then air dried for two days. The film produced was then peeled off and kept in a zipper bag and stored in a desiccator. Film without CNC was also prepared to serve as control (T0).

E. Characterization of Starch-CNCs biocomposite films

The surface morphology of the film was analyzed using scanning electron microscope (SEM). A dried section of the film was pressed onto a double-sided tape adhered to the sample holder surface and coated in gold. Imaging of each sample was done at an applied accelerating voltage and current of 10 kV and 10 μA, respectively using JSM-5310 scanning electron microscope.

Tensile properties which include the tensile strength and Modulus were determined using the ASTM D882-02 method. Films were cut manually into 1.5x10 cm and then stretched by Instron 5585H tensometer using at a crosshead speed of 12.5 mm/min. Testing conditions include relative humidity of 50±5 and temperature of 23±2°C. At least 7 samples per treatment were tested and values were averaged.

Moisture uptake tests were performed by subjecting 20 mm x 20mm films at two different relative humidities (RH) (70%RH using saturated NaCl solution and 40%RH using silica). The gain in weight of the film at 70% RH expressed as percentage of the original weight obtained at 40% RH served as a measure of moisture uptake of the films.

III. RESULTS AND DISCUSSION

A. Cellulose nanocrystal yield

Alkali treatment, both for garlic stalk and rice straw, yielded white cottony fibers as shown in Figure 1. Hydrolysis of these fibers produced a suspension of cellulose nanocrystals. The percentage of yield of CNC based from the raw garlic stalk and rice straw were found to be 4.6% and 6.6%, respectively.

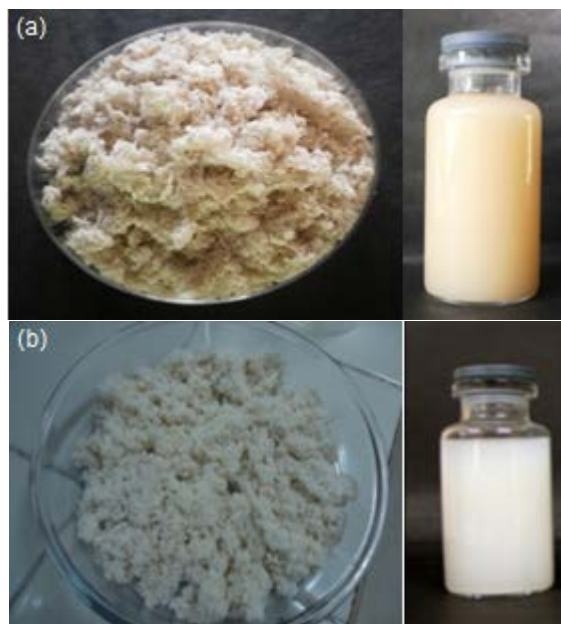


Fig. 1 The cellulose fibers after delignification and the CNC suspension after acid hydrolysis; (a) Garlic stalks (b) Rice straws.

Changes in the morphological structure of garlic stalk and rice straw are shown in Figure 2. The SEM image of the raw garlic stalks (Fig. 2a) does not show individualized cellulose fibers because of the presence of lignin and hemicelluloses that act as cementing components around the fiber bundles. These substances were removed during delignification as seen in the image for the delignified garlic stalk (Fig. 2b), which shows smaller, more separated, and more defined cellulose microfibrils. The cellulose fibers have an average diameter of $8.5 \mu\text{m}$. Also, the untreated rice straw (Fig. 2c) shows the cellulose fibers embedded in hemicelluloses and lignin which removed during delignification as seen in Fig. 2d which shows smaller and more defined cellulose fibers with an average diameter of $4.98 \mu\text{m}$.

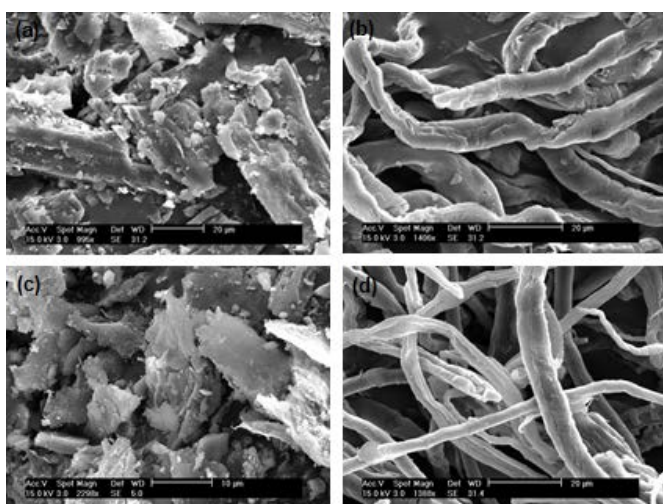


Fig. 2 SEM micrographs of raw and delignified garlic stalks (a, b) and rice straws (c, d).

B. Crystallinity

X-Ray diffraction was used to analyze the crystallinity of the isolated CNCs. The x-ray patterns of the raw and delignified sample were also obtained for comparisons. The changes in crystallinity of garlic stalk and rice straw before and after chemical treatment can be seen from the diffraction patterns presented in Figure 3(a) and 3(b), respectively. All diffractograms display two well-defined peaks around $2\theta=15^\circ$ and 22° , characteristic of cellulose. The appearance of a singlet peak at $2\theta=22^\circ$ for the isolated CNC confirmed that the isolated CNC was Cellulose I. Diffractogram of the isolated CNC gave the sharpest peak with the highest intensity, indicating highest crystallinity among the raw and delignified samples. This is due to the dissolution of amorphous zones of cellulose after acid hydrolysis [6]. During acid hydrolysis, the hydronium ions could penetrate into the amorphous regions of cellulose promoting the hydrolytic cleavage of glycosidic bonds and finally releasing the individual crystallites [7]. The computed crystallinity indices of the raw garlic stalk, delignified garlic stalk and CNC are found to be 40%, 55% and 62%, respectively. Whereas, the CNC from rice straw was more crystalline with computed crystallinity indices of 43%, 64% and 76% for the raw, delignified and acid hydrolyzed rice straw (CNC), respectively.

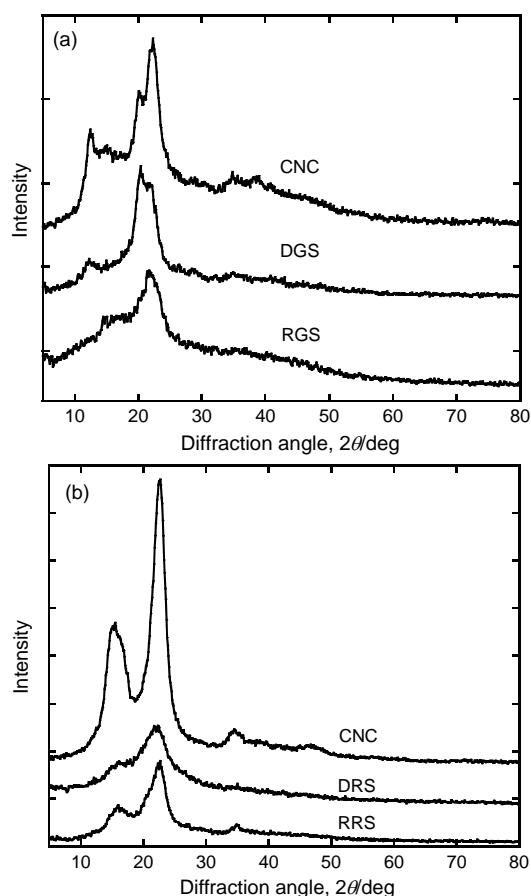


Fig. 3 X-ray diffraction patterns of raw, delignified and isolated CNCs from (a) garlic stalks (b) rice straws.

C. Morphology

Fig. 4(a) and 4(b) shows the TEM micrographs of the isolated cellulose nanocrystals from garlic stalk and rice straw, respectively. The isolated CNCs from garlic stalk appear as black, spherical spots in the micrograph. The isolated CNCs were found to have diameters ranging from 30-50 nanometers. The calculated value for the average diameter of the CNCs was 35 nm. On the other hand, short, rod-like cellulose nanocrystals with smaller diameter ranging from 10-12 nm were obtained from rice straw. It can be observed that the CNCs are highly aggregated, with some particles overlapping each other. Habibi et al., [8] mentioned that aggregation of particles occurs during the drying step of the preparation of test specimens for TEM. Aggregation of cellulose nanocrystals can be attributed to strong hydrogen bonding of the particles. Lu and Hsieh [9] suggest that the strong H-bonding among cellulose nanocrystals overcomes the repulsion of surface negative charges when CNC is in the dry phase.

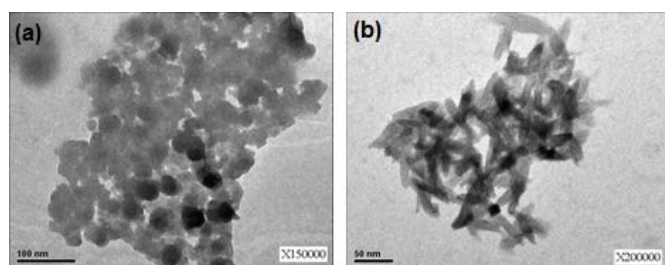


Fig. 4 TEM images of CNCs obtained from garlic stalks (a) and rice straws (b).

D. Starch-CNC biocomposite films

SEM micrographs of the surface and cross section of the biocomposite films without or with CNCs from garlic stalk and rice straw are shown in Fig. 5(a-f). All films show smooth surfaces and homogenous dispersion of the CNCs in the starch matrix. According to Cañigueral et al. [10], the accuracy of SEM cannot be enough for the clear determination of filler dispersion in the film because only poor dispersions would be easily detected by this technique. One way to confirm good quality of filler dispersion is the enhancement of mechanical properties.

E. Mechanical Properties

The mechanical properties of the prepared biocomposite films are summarized in Table 2. For films reinforced with CNC from garlic stalks, reinforcement was found to be optimum at a starch to CNC ratio of 100:5. Compared to non-reinforced film (T0), tensile strength increased by 56% and 34%, respectively. The improvement in tensile strength is mainly a function of filler dispersion and adhesion between interfaces of filler and matrix [10]. Good interfacial adhesion between starch and CNCs are expected since both contain hydroxyl groups that can form hydrogen bonds between interfaces. The strong H-bonding between interfaces of CNCs and starch results to the formation of a rigid network of CNCs causing the effective reinforcement of the matrix [11]. Increasing the amount of CNC, however,

resulted to deterioration in mechanical properties. This result could be attributed to possible aggregation of CNC.

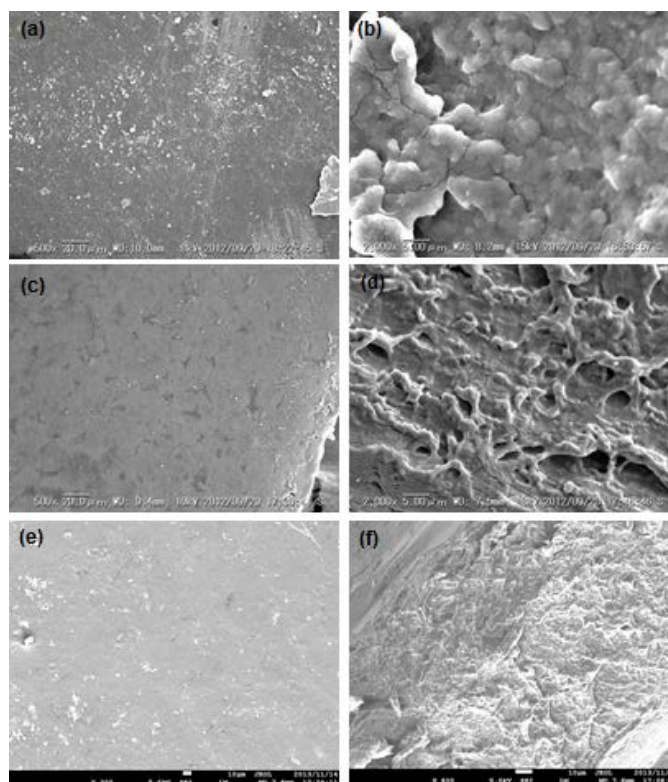


Fig. 5 Surface and cross sectional SEM images of CNCs reinforced bioplastic; Without CNCs (a: surface, b: cross section); With garlic stalk CNCs (c: surface, d: cross section) at a (starch:CNCs) ratio of (100:5); With rice stalk CNCs (e: surface, f: cross section) at a (starch:CNCs) ratio of (100:10).

Films reinforced with CNC from rice straw showed better mechanical properties than that reinforced with garlic stalk-CNC. Moreover, increasing the amount of rice straw-CNC improved both the tensile strength and Modulus. At starch to CNC ratio of 100:10, tensile strength and modulus were more than double the non-reinforced film. The better reinforcing effect of rice straw-CNC can be attributed to its smaller size, rod shape, and higher crystallinity.

TABLE II
MECHANICAL PROPERTIES OF STARCH-BASED BIOPLASTIC WITH VARYING AMOUNT OF CNCs FROM GARLIC STALK AND RICE STRAW.

Treatment (starch:CNCs)	Tensile Strength (MPa)		Modulus (MPa)	
	Garlic Stalk	Rice straw	Garlic Stalk	Rice Straw
T0(100:0)	10.0	10.0	327.3	327.3
T1(100:2.5)	14.3	13.9	416.2	531.0
T2(100:5)	15.6	14.0	439.6	504.0
T3(100:10)	10.5	26.8	392.5	898.0
T4(100:15)	9.58	26.0	349.98	896.0

Moisture uptake of films generally decreased with the addition of CNC (data not shown). The decrease in water uptake can be due to the strong interfacial adhesion between cellulose and starch. Starch and cellulose both contains hydroxyl groups

that can form hydrogen bonds. The resulting hydrogen-bonded network of cellulose with the starch in the composite could prevent the formation of voids where water molecules can pass through [11].

IV. CONCLUSIONS

Cellulose nanocrystals can be isolated from garlic stalk and rice straw through alkali treatment and acid hydrolysis. The morphology and crystallinity of the isolated CNCs varied for each sample. Spherical cellulose nanocrystals with an average diameter of 35 nm and crystallinity of 62% can be isolated from garlic stalks while short, rod like cellulose nanocrystals with diameters of 10-12 nm and crystallinity of 76% can be isolated from rice straw. Starch-based bioplastic films can be prepared by solution casting with the isolated CNC as reinforcing filler. Improvement in mechanical properties was higher for films reinforced with rice straw CNC than those with garlic stalk CNC.

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