Microcrystalline Cellulose and Biocomposite from Kapok (*Ceiba pentandra)*: Characterization and Fabrication

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ABSTRACT

Plastic is the most commonly used material in every industry around the world. Due to increasing demand in the food packaging industry, innovations in plastic manufacturing utilizing other raw materials is ventured. Polyvinyl alcohol (PVA), a synthetic water-soluble polymer known for its film-forming, emulsifying and adhesive property, is known to be an alternative raw material for plastic manufacturing. However, PVA alone is too costly, so blends are used to lower the cost of producing PVA films. To make the plastics strong, water resistant, and biodegradable, reinforcements like cellulose fibers and starch are considered.

This study aims to prepare and characterize the micro cellulose fiber and biocomposites from kapok (*Ceiba pentandra)*. The micro cellulose fiber was obtained through a series of chemical (alkali treatment, bleaching and acid hydrolysis) and mechanical treatments. Analysis of the FTIR spectrum of the cellulose fibers revealed the presence of lignin and hemicellulose peaks from the untreated fiber and its disappearance after chemical and mechanical treatment. Size and surface morphology analysis revealed a rod and granule-like structure with sizes ranging from 9 to 24 μm. Biocomposite films were prepared by mixing varied amounts of the cellulose fiber (0,5, 10, 15 and 20 wt%) polyvinyl alcohol (PVA), water, and glycerol and were casted in a petri dish. Physico-mechanical tests of the biocomposite films showed increase in tensile strengths and % elongation. Significant differences were noted in the physical properties among the biocomposite films.

Keywords: Ceiba pentandra, Cellulose fiber, Biocomposites

1. INTRODUCTION

Plastic is a widespread and pervasive material in the Philippines, in the electronics, construction, food, cosmetics, packaging, and automotive industries [1]. Increasing demand for plastic requires not only meeting the supply but also ensuring the quality (water resistant, low cost good specific mechanical properties, and low density) and complying with the laws on biodegradability. Polyvinyl alcohol meets the demands of plastic particularly in the food packaging industry but PVA alone when utilized is too expensive. Blends are used to lower the cost of producing PVA made films [2].

To make the plastic strong, water resistant and biodegradable, other reinforcements are considered like the cellulose fiber [2],[3],[4]. Cellulose fibers are isolated or obtained from plants such as banana peels [4], empty fruit bunch fibers [2], cassava bagasse [5], and coconut coir fibers [6].

One of the plants which is a potential source of cellulose fibers from the *C. pentandra* as it is rich in cellulose which is about 35% [7]. It is slender and deciduous and bears an oblong, soft, and wooded pod-bearing dicot fruit. The trees are planted in settled areas throughout the Philippines. The fiber is yellowish to light brown, odorless, and fluffy. In the Philippines, the fibers obtained from the fruit are commonly used as filling materials for pillows, cushions and mattresses, and in the manufactures of buoys and life saving devices at sea due to its excellent buoyancy and air-filled lumen. It can also be used as cotton substitute in surgeries and can be mixed with other fibers for the manufacture of textiles [8],[9]. In the Philippines, the average yield of *C. pentandra* is 450 kg of dried floss per hectare [8].

With this information, the researchers aimed to produce a biocomposite film that can be used as a potential alternative to plastics.

This study aimed to prepare and characterize the cellulose fiber and biocomposites from *C. pentandra*. The biocomposites with natural fibers will give boost in the utilization of *C. pentandra* as one of the natural fibers thus, enhance its economic value. The research finds relevance to environment advocates as it will help in the possible reduction of waste. This can help minimize the environment pollution by adding the biocomposite as an option to be utilized as a packaging material. Since biocomposites have biodegradability characteristics, problems with plastics ending up in landfills and bodies of water will be minimized.

Objectives of the study

The aim of the study is to prepare and characterize the cellulose fiber and biocomposites from *C. pentandra*. Specifically, it sought answers to the following questions:

1. What are the functional groups present in the untreated and treated fibers of *C. pentandra*?
2. What are the characteristics of the cellulose fiber in terms of :
   - 2.1. size
   - 2.2. surface morphology

3. What are the physical characteristics of the prepared biocomposites with 0, 5, 10, 15, 20 % (w/w) cellulose fiber in terms of the following:
   3.1. thickness
   3.2. density
   3.3. moisture content
   3.4. tensile strength
   3.5. % elongation / elongation at break
   3.6. water absorption property
4. Are there significant differences in the physical characteristics of the prepared biocomposites?

2. MATERIALS AND METHODS

Collection and reparation of samples

The fibers of *Ceiba pentandra* were collected from a dried fruit bunch in Kumintang Ibaba, Batangas City. The fibers were carefully cleaned to remove adhering seeds, dirt, and other plant matter.

Preparation of cellulose fibers

Cellulose fibers from *C. pentandra* were obtained by chemical treatments and subjected to mechanical treatment using experimental procedure for the preparation of cellulose fibers described by [5] with some modifications. About 10 grams of fibers of *C. pentandra* was subjected to alkali treatment (600 mL, 4% wt. KOH) to purify the cellulose and eliminate lignin and hemicellulose. The mixture was transferred to a beaker and subjected to heat (80°C) for 1 hour. After the alkali treatment, the fibers were filtered and washed with distilled water. The treatment was performed twice, before and after the bleaching process.

The bleaching process followed after the alkali treatment. This was done by the addition of 10% (v/v) acetic acid, sodium hypochlorite (bleach with 4.5% concentration by volume) in a 1:1 ratio (total volume of 500 mL). The process was carried at 70°C for 1 hour. The mixture was filtered and washed with distilled water. The bleaching process was repeated twice.

Acid hydrolysis, using 50% sulfuric acid (about 200 mL), was done after the bleaching process. The process was carried at a temperature of 60°C for 1 hour with continuous stirring. The material after hydrolysis was washed by centrifugation at 4000 rpm for 12 minutes and 30 seconds. The process was repeated several times by adding distilled water until the pH of the material (pulp) reached a range of 5-6. The extracted cellulose fiber was subjected to sonication for 30 minutes. Mechanical treatment was conducted by subjecting a small amount of the sample in a blender for 30 minutes. The cellulose suspension that was obtained after treatment was kept in a refrigerator prior to preparation of biocomposite.

Determination of functional groups in the untreated and treated fibers of *C. pentandra*

Functional group was determined using an FTIR (Thermo Scientific Nicolet 6700 FT-IR) spectroscope. FTIR confirms whether the stretch bands representing hemicellulose and lignin were removed or minimized after the chemical treatments of the fibers of *C. pentandra* [4].

Determination of size and surface morphology

A field emission scanning electron microscope (FESEM, Dual Beam Helios Nanolab 600i) was used to determine the size and surface morphology of the cellulose microfiber .

Preparation of biocomposite films

The biocomposite films were prepared by mixing polyvinyl alcohol (PVA), water, glycerol, and cellulose fiber. The film was prepared by casting the solution in a Petri dish.

The PVA solution was prepared by dissolving PVA (10% wt.) powder in 90 ml of distilled water at 95°C for 30 minutes. The solution was homogenized by mechanical stirring until all the PVA granules were completely dissolved in water.

After the PVA was dissolved, glycerol was added to the solution at a 30% wt. ratio based on the total weight of PVA. 5 sets of biocomposites (10 specimens per set), with a cellulose fiber content of 0, 5, 10, 15, 20 % (w/w) based on the weight of PVA solution were prepared. A solution of 5g mixed polymer was cast on a petri dish plate and allowed to dry at room temperature for two (2) days. After the film was completely dry, the film was peeled off from the plate.

Determination of thickness

The thickness of the biocomposites was measured using a manual micrometer.

Determination of density

The density of each biocomposite was measured by cutting each film into 20 x 20 mm squares, and the thickness was then measured. The samples were dried at 105°C for 24 hours and then weighed. The density was calculated as the ratio between the weight and volume *(thickness x area)* of the biocomposite film [4].

Determination of moisture content

Moisture content was determined using the gravimetric method of analysis, particularly by the oven method. Percent moisture was determined using the formula:

$$\%\ Moisture = \left(\frac{W_f - W_i}{Wi}\right) 100 \quad (1)$$

where, W_f is the weight of the sample after oven drying and W_i, the wet weight of the sample after drying.

The moisture content of the films was analyzed gravimetrically, in triplicate, by drying the samples at 105°C for 24 hours as described in ASTM D644-99 [4].

Determination of mechanical properties

The tensile strength and elongation at break (% elongation) of the biocomposite were tested in accordance with ASTM D638/D882 with 8 samples per set of biocomposites with cellulose fibers. The analysis was done using a Universal Testing Machine (Model 5585H Instron UTM). The set up was carried using a 100 N pneumatic grip with a maximum pressure of 6 bars.

Water absorption capacity

Water absorption capacity is the measure of the water absorbed by a material in terms of percent and is determined using the formula.

$$W_{Absorption\ Capacity} = \left(\frac{W_f - W_i}{Wi}\right) 100 \quad (2)$$

where, W_f is the weight of the film after being immersed in water and W_i, is the initial weight of the film before the immersion in water.

Water absorption was done by immersing the sample in distilled water for 5 minutes after the sample was dried in an oven at 50˚C [2][10].

Data Analysis

One-way analysis of variance (ANOVA) was used to compare the physical characteristics of biocomposite films with varying amount of cellulose. One-way ANOVA was done using IBM SPSS ver. 22.

3. RESULTS AND DISCUSSION

Functional group analysis of the untreated and treated cellulose fibers

Figure 1 shows the spectral peaks at 3500 to 3200 cm^{-1} on the untreated and treated fiber which denote the free O-H stretching vibration in cellulose molecules [5] [11][12] or that the spectral bands of 3175- 3490 cm^{-1} denotes the O-H stretching of the intramolecular hydrogen bonds of cellulose I [13]. The spectral peaks were in the range 1505 -1597 cm^{-1} corresponding to the aromatic skeletal vibration, indicating the presence of lignin on the untreated fiber.

In addition, on the untreated fiber, hemicellulose and lignin presented a characteristic peak in the range of 1739 cm^{-1} which corresponds to C=O stretching. This peak substantially disappeared in the spectra of treated cellulose fiber due to the removal of hemicellulose related to the purification and acid hydrolysis used [14].The 2919 cm^{-1} region in cellulose and hemicellulose were due to the aliphatic saturated C-H stretching vibration [6]. The absence of the absorption bands at peak 1597 cm^{-1} related to aromatic ring stretch indicates the removal of lignin [14] after subjecting to bleach and alkaline treatment. The peak at 1375 cm^{-1} corresponds to the C-H asymmetric deformation of cellulose and lignin [14] in the treated

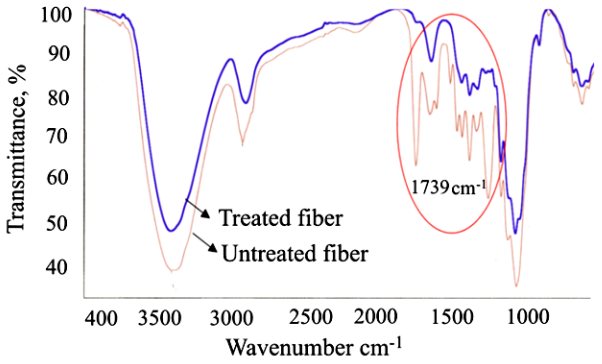

Figure 1. FTIR spectrum of the *C. pentandra* fiber before and after treatment.

fiber. The band at 1645 cm^{-1} may be due to the absorbed water of the cellulose in the untreated and treated fibers [2]. The peak in the range of 1117-1247 cm^{-1} shows stretching of C-O and O-H and deformation bands in cellulose, hemicellulose and lignin [6]. From these FTIR results, it can be seen that the constituents like lignin and hemicellulose were removed after chemical and mechanical treatments.

Surface morphology and size of treated cellulose fiber

Figure 2 shows agglomerated rod-like structures of the treated fibers. The rod-like structure was generated by acid hydrolysis treatment.

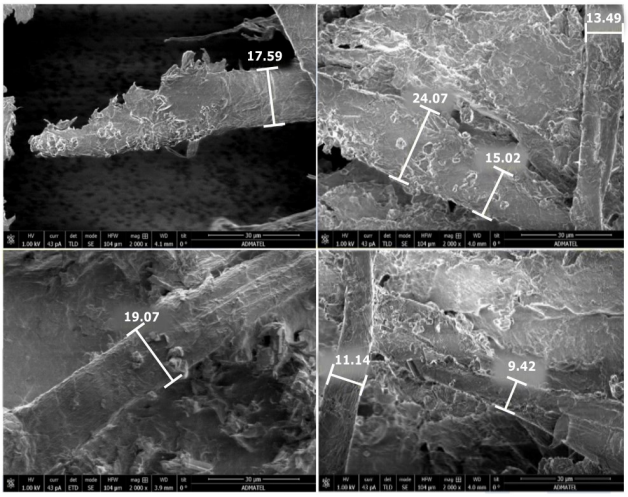

Figure 2. SEM images of the cellulose fibers at 2000 x

The alkali treatment at high temperature helps to hydrolyze hemicellulose. Bleaching on the other hand helps to remove most of the lignin which is believed to be linked with the carbohydrate moiety of two types of linkages, sensitive and insensitive linkage to alkali treatment). The sensitive linkage to alkali forms an ester type of combination between the hydroxyl and carboxyl group of the uronic acid hemicellulose. The other linkage is hydroxyl-hydroxyl; the degradation of lignin can lead to the formation of hydroxyl, carbonyl and carboxylic groups, which can help to solubilize the lignin content in the alkali reagent for the extraction of cellulose [5]. The morphological

structure and size of the fibers changed due to the removal of the amorphous regions of the cellulose by the treatment [15].

The images show that the diameters of the treated fibers were in the range of approximately 9 to 24 μm. At this point, the researchers obtained cellulose microfibers after subjecting the fibers to chemical and mechanical treatments. The chemical and mechanical treatments affected the size and decreased it into micro-particle size.

Physical characteristics of the cellulose biocomposite films

Table 1 presents the physical characteristics of the biocomposite films with 0, 5, 10, 15, 20 %(w/w) cellulose fibers. Physical properties include thickness, density, moisture content, tensile strength, % elongation, and water absorption property.

The thickness values of the biocomposites with 0, 5, 10, 15, and 20 % (w/w) cellulose fiber were 30 ± 6.45 μm, 460 ± 6.45 μm, 470 ± 12.91 μm, 480 ± 10 μm and 500 ± 10 μm, respectively. The film with the highest thickness was BC20 while the film with the lowest thickness was BC0. BC20 has a favorable thickness because of its high cellulose fiber content compared to other prepared biocomposites. Upon the addition of cellulose content in the biocomposite films, the thickness of the films increased which suggests that a considerable amount of air was trapped during composite preparation [16].

The density values of the biocomposites with 0, 5, 10, 15, and 20 % (w/w) cellulose fibers were 2.95 ± 0.76 g/cm^3, 0.26 ± 0.04 g/cm^3, 0.24 ± 0.01 g/cm^3, 0.18 ± 0.05 g/cm^3 and 0.08 ± 0.02 g/cm^3, respectively. The prepared biocomposites with the highest density was found to be at BC0 of 2.95 g/cm^3. Cellulose fiber was found to have lower density [2][17]. It can be seen that the density decreased as the amount of cellulose fiber in the film increased. It can also be noted that as the thickness of the biocomposite increased, the density of the biocomposite decreased. Similar trend was cited and observed by [16]. In general, biocomposites are characterized as having low densities.

The moisture content values of the biocomposites with 0, 5, 10, 15, and 20 % (w/w) cellulose fibers were 8.78 ± 0.59 %, 12.91 ± 0.46 %, 20.67 ± 2.86 %, 29.46 ± 2.32 % and 33.95 ± 0.3 %, respectively. The film with the highest moisture content of 33.95% was found at BC20. It can be noted that as the cellulose fiber content of the film increased, the moisture content also increased. The moisture absorption of the composites based on natural fibers is generally high [17]. In addition, cellulose fiber is compatible with polar matrices, like polyvinyl alcohol, which give higher moisture content. An increase in the percentage of cellulose content increases the number of available hydroxyl groups which enhances the moisture content [15]. The absorption of moisture by biocomposites lowers the mechanical properties of the biocomposites [18].

The observed tensile strength values of prepared biocomposites were 9.31 MPa, 9.34 MPa, 16.95 MPa, 11.59 MPa, and 12.81 MPa for BC0, BC5, BC10, BC15 and BC20, respectively. The film with the highest tensile strength of 16.95 MPa occurred at BC10 and with the lowest tensile strength, 9.31 MPa was BC0. When the cellulose fiber content exceeded BC10, the tensile strength of the film tended to decrease as the cellulose fiber content increased. A similar study [2] showed the tensile strength of blend films tended to increase from 0% to 10% (v/v). When the cellulose content exceeded 10% (v/v), the tensile strength of the film decreased along with an increasing cellulose content. The trend of the present study has similarities with the study of [19] wherein the researchers obtained the highest tensile strength at 10% with unmodified fiber to thermoplastic starch was 3329%.

It could be observed that the trend for the % elongation was the same as the trend of tensile strength. The % elongation values of the prepared biocomposites were 286.5%, 364.43%, 415%, 296.29%, and 366% for BC0, BC5, BC10, BC15 and BC20, respectively. It was found that the highest elongation at break (%) was at BC10 which is around 415% in comparison with the BC0 which had 298.5%. An addition of cellulose fiber that exceeds BC10 gives a deterioration effect for the elongation at break from 415% to 296.29%. The elongation at the break of biocomposite film increased from 296.29% to 366% along with the increase of cellulose fiber content.

Table 1. Physical characteristics of the biocomposite films mixed with various amount of cellulose fibers.

Amount of cellulose fiber in biocomposite (BC), %		Properties, mean±SD					
		Thickness (mm)	Density (g/cm^3)	Moisture (%)	Tensile strength (mPa)	Elongation at break (%)	Water absorption (%)
BC0	0	30±6	2.95±0.76	9±0.59	9±3	287±123	83±7
BC5	5	460±6	0.26±.0.04	13±0.46	9±4	364±78	178±17
BC10	10	470±13	0.24±0.01	21±2.86	17±7	415±94	262±29
BC15	15	480±10	0.18±0.05	30±2.32	12±4	296±73	337±14
BC20	20	500±10	0.08±0.02	34±0.30	13±4	366±87	327±41
One-way ANOVA		F=1603, p<0.05	F=26, p<0.05	F=80, p<0.05	F=3, p<0.05	F=2, p>0.05	F=91, p<0.05

The enhancement in tensile strength and elongation at break at low content of fillers could be due to the very fine nature of cellulose fiber and well dispersion of cellulose through the biocomposites. The reason for the reduction of tensile strength and elongation at break could be that the excess amount of cellulose fiber led to an increase in intermolecular interaction that might compete with interactions among PVA, starch, and cellulose fiber. Therefore, the miscibility and compatibility of PVA and cellulose were reduced, which decreased the tensile strength and elongation at break of composite films [2].

The water absorption values of the biocomposites with 0, 5, 10, 15, and 20 % (w/w) cellulose fibers were 82.85 ± 6.94 %, 178.10 ± 16.51%, 262.36 ± 28.59 %, 336.93 ± 14.44 % and 327.22 ± 40.72 %, respectively. The water absorption capacity increased as the amount of cellulose content increased. The water absorption capacity of the BC0 had a lower value than the biocomposite film with cellulose fiber content. This indicates that the presence of cellulose fibers in the films improves the water absorption capacity. The presence of the cellulose fibers means that the pathway for water molecules to diffuse into the composites is altered from the direct diffusion to a tortuous path, which improves water barrier properties. The formation of some large accumulated cellulose particles generates voids that can absorb water molecules and therefore increase the percentage of water absorption [2]. From this, it can be inferred that the prepared biocomposites easily deteriorate when subjected to an aqueous environment. This means that the prepared biocomposites are not suitable for applications with water.

Comparison of the physical characteristics of the cellulose biocomposites films

The physical properties of the prepared biocomposite films were statistically compared from one another (Table 1). Results showed that the p-value of the physical properties, in terms of thickness, density, moisture, tensile strength, and water absorption, of the prepared composites with cellulose fibers are less than 0.05. Therefore, there are significant differences in the thickness, density, moisture, tensile strength and water absorption of the prepared biocomposites with varying amounts of cellulose fibers. This indicates that the behavior of the film when analyzed for the said properties varied with increasing cellulose content. Thus, it can be inferred that the addition of cellulose fiber greatly affected the physical properties of the biocomposites.

The % elongation of the prepared biocomposites with varying amounts of cellulose fibers has a p-value of 0.098 and is higher than á= 0.05. Thus, the null hypothesis was accepted, and therefore, there is no significant difference in the % elongation of the prepared biocomposites with varying amounts of cellulose fibers. With this result, it can be deduced that the addition cellulose fibers has no significant effect on the % elongation of the biocomposite films.

4. CONCLUSIONS

The following conclusions were drawn based on the results of the analysis:

1. The functional groups present in the untreated and treated cellulose fibers are alcohol, alkene, ester, aromatic carbon, and carbonyl group; the FTIR spectrum of the cellulose fibers shows the presence of lignin and hemicellulose from the untreated fiber and the disappearance of the peak after chemical treatment.

2. Cellulose fiber is micro sized with rod and granule-like surface structure.

3. BC20 has the highest thickness and moisture content; BC0, the highest density; BC10 has the highest tensile strength and % elongation; and BC15 has the highest water absorption.

4. The physical properties of the biocomposite films with varying amounts of cellulose fibers manifest significant differences in physical properties in terms of thickness, density, moisture, tensile strength, and water absorption except in % elongation.

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ACKNOWLEDGEMENTS

The researchers would like to extend their gratitude to Batangas State University College of Arts and Sciences Laboratory and DOST-ADMATEL.