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Research Article

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Properties of beechwood xylan films reinforced with bamboo (*Bambusa blumeana* J.A. & J.H. Schultes) cellulose nanowhiskers

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ABSTRACT

The objective of the study was to prepare films made from Beechwood xylan reinforced with varying amounts of cellulose nanowhiskers extracted from a Philippine-grown bamboo species (Bambusa blumeana J.A. & J.H. Schultes). The effect of varying the concentration of bamboo cellulosic nanowhiskers on various properties of the xylan film, such as grammage, bulk density, thickness, rupture strength, water vapor transmission rate and smoothness of the film surface was determined. The morphology of the nanocomposite films was evaluated via Atomic Force Microscopy which showed increasing film surface roughness at higher cellulosic nanowhisker loading.Varying the concentration of the nanowhiskers does not have a significant effect on the grammage, bulk density and thickness of the resulting films. However, the rupture strength of the films increased significantly with increasing nanowhisker content. The highest rupture strength (23,121.23 Pa) was obtained in the film with 10% nanowhiskers. Furthermore, the water vapor transmission rate of the films decreased significantly with increasing nanowhiskers content, although the lowest recorded value of 0.9594 g-mil/m2-day was obtained for the filmwith 5% nanowhiskers reinforcement. Thus, small addition of bamboo nanowhiskers in the fabrication of xylan film can significantly improveproperties desirable in materials to be used for packaging.

Keywords: cellulose nanowhisker, nanocomposite, xylan film, *Bambusa blumeana*, water vapor transmission

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INTRODUCTION

Packaging materials play an important role in ensuring that the products contained inside a package are protected from damage caused by contaminants and other external factors. In addition, the packaging material provides convenience in shipping and handling as well as in communicating to the prospective users, information about the product [1]. Demand in the use of biodegradable packaging materials is increasing as consumers are becoming more and more concerned about the impacts of their actions on the environment.

One recent trend in the production of environmentally-friendly packaging is the production of films based on natural polymers. Natural polymers, examples of which are starch, cellulose and hemicelluloses, are renewable and abundant in nature. Specifically, xylan films are receiving increasing attention asthey exhibit good film-forming properties and they can be readily modified by incorporating various additives into the matrix.

Xylan films made from barley husks exhibited good tensile properties; however, the resulting end products were initially brittle [2]. To enhance the properties of xylan films, reinforcement materials have been used as additive, an example of which is cellulose nanowhiskers. For example, oat spelt xylan films reinforced with cellulose nanowhiskers were prepared [3], and significantly improved tensile strength and water vapor transmission rate of the films was reported with the addition of the cellulose nanowhiskers.

The present study explores the use of cellulose nanowhiskers extracted from a species of bamboo growing in the Philippines, *Bambusa blumeana* J.A. & J.H. Schultes, locally known as "Kawayan tinik," as reinforcement in the fabrication of a film from commercial Beechwood xylan. This contributes to efforts to develop alternative materials from renewable resources, as well as in finding novel products that can help spur value adding of bamboo, otherwise a low-value plant species that is important to poor farmers and households.

EXPERIMENTAL SECTION

Materials: Beechwood xylan and D-sorbitol were purchased from Sigma-Aldrich. Bamboo pulp was prepared from a Philippine-grown Kawayan tinik (*Bambusa blumeana* J.A. & J.H. Schultes).

Preparation of Cellulose Nanowhiskers: Four hundred **(**400) g of skinned bamboo culm was cut into toothpick-sized sticks and pulped in a Kraft process following previously reported methodology [4] with some minor modifications. Bleaching using a hypochlorite, alkali extraction, and a second hypochlorite treatment(HEH) sequence was used to bleach the Kraft pulp in accordance with the methodology outlined by Karlsson. [5]. A portion (3 g) of the resulting bleached pulp was then taken for the preparation of alkali-insoluble cellulose, the process consisting of adding to the bleached bamboo pulp, 60 mL of 15.6% carbonate-free sodium hydroxide solution for 30 minutes and washing the pulp with distilled water and acetic acid. In the acid hydrolysis reaction to produce nanowhiskers, 0.5g of oven-dried alkali insoluble-cellulose pulp was added to 50 mL of 46% v/v sulfuric acid at 40°C for 30 minutes. Five hundred (500) mL of distilled water was added to the mixture to stop the hydrolysis reaction. The reaction mixture was neutralized using 10% NaOH solution and then centrifuged at 10,000 rpm for 10 minutes. The precipitate containing the nanocellulose fraction was suspended in water and then sonicated for 1 hour in a Cole-Parmer Ultrasonicator and freeze-dried in a LabConco Freeze-Drier.

Preparation of Nanocomposite Films: Varying amounts of cellulose nanowhiskers corresponding to 2%, 5% and 10% w/w of the total solids in the film and xylan and sorbitol in a 40-60 ratio were added to 35mL of distilled water and heated at 95°C for 15 minutes. The mixture was then casted in Teflon dishes and allowed to dry overnight in an oven set at 40°C.

Water Vapor Transmission Rate Determination: A modification of ASTM E 96-95[6] wet cup method was used to determine water vapor transmission across the film. The nanocomposite film was attached, using a cyanoacrylate adhesive, to the surface of the glass bottle filled with distilled water. The entire set-up was placed in a conditioning oven set at 37°C and 50% relative humidity (RH) and the change in weight of the set-up was monitored for 24 hours. The water vapor transmission rate was calculated by dividing the mass of the water lost by the product of time and area of the dish.

Mechanical Testing: Film samples were cut into 3.81cm by 1.27 cm sizes according to ASTM D1708 [7]. The film samples were tested using an Instron 4411 Universal Testing Machine at a crosshead speed of 5mm/min. From the data for the applied load and displacement of the sample, the stress-strain curve was generated and the rupture strength of the sample was determined.

Atomic Force Microscopy Analysis: Nano-scaleimages of the bamboo cellulosic nanowhiskers and of the surface of the nanocomposite films were taken using a Park Systems XE70 Atomic Force Microscope (AFM)available at the Institute of Chemistry, College of Arts and Sciences, University of the Philippines Los Baños. The samples were analyzed in non-contact mode using point probe plus non-contact cantilever with resonant frequency of 330 KHz and nominal force constant of 42 N/m. Prior to imaging, the film samples were cut into 1 cm^2 sizes and were mounted on sample stubs using double-sided adhesive tape. An AFM image was taken for the control film as well as for each of the xylan nanocomposite films with varying concentrations of nanowhiskers.

RESULTS AND DISCUSSION

Variations in the length of the bamboo cellulose nanowhiskers (Figure 1)were observed upon AFM analysis which was attributed to the uneven length of the crystalline and amorphous regions in the *in situ* structure of cellulose [8]. The width of the cellulose nanowhiskers was 27.24 nm which was within the 5-30nm range of the width of nanowhiskers from wood as specified in the work of Saxena et al. [8].

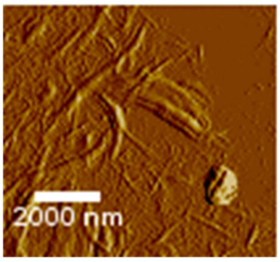
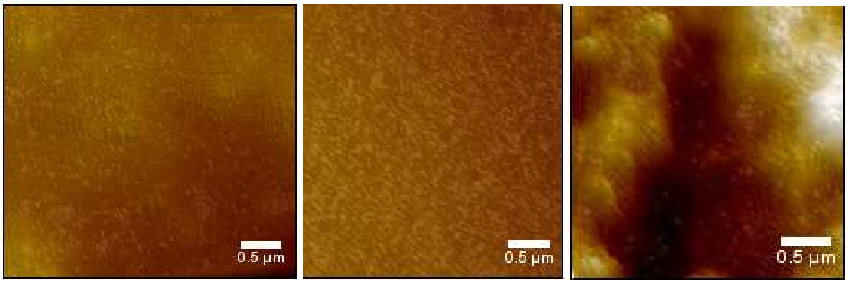


Fig.1. Atomic Force Microscopy Image of Bamboo Cellulosic Nanowhiskers

The measured length of the cellulose nanowhiskers was 1271 nm, which was wider than the width range of 100-300 nm as reported for wood nanocellulose [8]. Among others, this indicates the higher degree of crystallinity of cellulose in bamboo relative to wood pulp. The Atomic Force Microscopy images of the xylan films reinforced with varying concentrations of cellulose nanowhiskers (CNW)are shown below:



a b c

Fig.2. Atomic Force Microscopy Image of (a) Xylan control film (0% CNW); (b) Xylan film reinforced with 2% CNW; (c) Xylan film reinforced with 10% CNW

Increasing amounts of cellulose nanowhiskers within the xylan films lead to decreasing film surface smoothness as seen above. At 10% CNW loading, agglomeration was observed at the surface of the film, contributing to increased surface roughness. In addition, thisresulted in a more open structure of the film which led to faster water vapor transmission rate of the film reinforced with 10% CNW (Table 1).

Table 1. Normalized Water Vapor Transmission Rates (WVTR) of the Nanocomposite Films reinforced with different levels of bamboo cellulosic nanowhiskers (CNW).[1]

XYLAN FILM SAMPLE	WVTR[2]
Control with 0% CNW	23.06 ± 6.25[a]
Reinforced with 2% CNW	1.04 ± 0.14[b]
Reinforced with 5% CNW	0.96 ± 0.30[c]
Reinforced with 10%CNW	1.05 ± 0.16[d]

[1] *Means with a common letter are not significantly different at P = 0.05*
[2] *Water vapor transmission rate, in g-mil/day-m^2*

Increasing the amount of cellulose nanowhiskers within the film has a positive effect on the film's rupture strength. Specifically, the highest rupture strength (23,121.23 Pa) was observed at 10% CNW loading (Figure 3). However, the rupture strength of the films was lower as compared to the mechanical strength of xylan films as reported by [8]. This can be attributed to the higher amounts of plasticizer used which according to [9]was found to reduce the mechanical strength of the films.

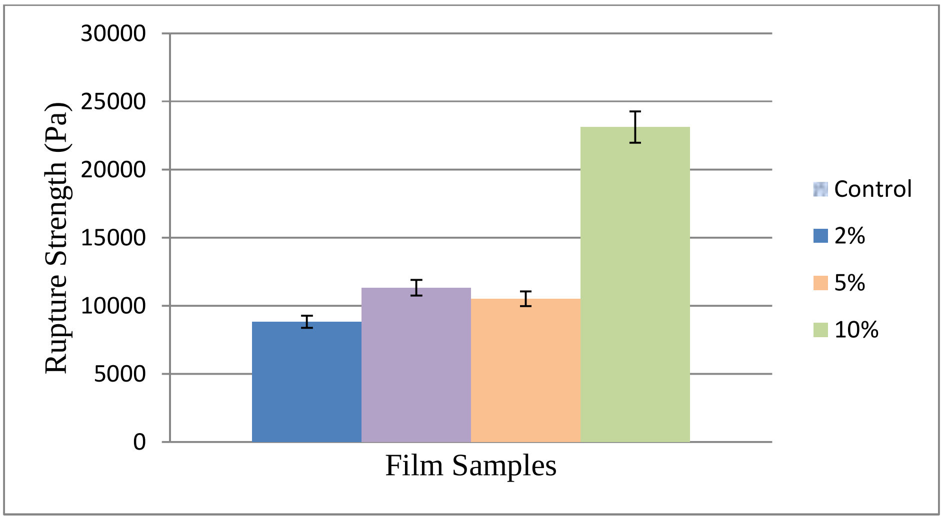


Fig.3. Rupture Strength of Xylan Nanocomposite Films Reinforced with Different Levels of Bamboo Cellulosic Nanowhiskers (CNW)

Table 2 summarizes the grammage, thickness and bulk density of the films.

Table 2. Grammage, Thickness and Bulk Density of the Beechwood Xylan Films Reinforced with Different Levels of Bamboo Cellulosic Nanowhiskers (CNW).[1]

XYLAN FILM	THICKNESS (mm)	WEIGHT (g)	GRAMMAGE (g/m^2)	DENSITY (g/cm^3)
Control (0% CNW)	0.41[a]	0.56[b]	329.75[c]	0.81[d]
Reinforced with 2% CNW	0.45[a]	0.51[b]	300.31[c]	0.67[d]
Reinforced with 5% CNW	0.44[a]	0.54[b]	317.98[c]	0.72[d]
Reinforced with 10% CNW	0.40[a]	0.54[b]	317.98[c]	0.82[d]

[1]*Means with a common letter are not significantly different at P = 0.05*

The grammage, thickness and bulk density of the films were not significantly different from each other, which was attributed to the constant solids to liquid ratio of the materials used in forming the nanocomposite films.

The observed increases in the mechanical strength and barrier properties of the nanocomposite films were consistent with the 1.5% calculated percolation threshold of bamboo cellulose nanowhiskers using the formula derived in an earlier study [9]. Furthermore, the increase in the mechanical and barrier properties of the films was attributed to the formation of a percolation network of cellulose nanowhiskers [8].

CONCLUSION

Increasing bamboo cellulosic nanowhiskers concentration within fabricated xylan film decreases the smoothness of the films due to agglomeration of the cellulose nanowhiskers observed at higher CNW concentrations. The highest water vapor transmission rates of the films was observed at 5% CNW concentrations. But beyond this loading, the water vapor transmission rate of the films increased, which could be the result of the agglomeration of CNW at higher loading rates. On the other hand, increasing the CNW loading within the film has a positive effect on the mechanical strength as the highest rupture strength of the xylan film was recorded at 10% CNW concentration. Lastly, incorporation of varying amounts of cellulose nanowhiskers was found to have no significant effect on the density, thickness and grammage of the resulting films. Thus, bamboo cellulosic nanowhiskers can be used to enhance desired properties in packaging materials without significantly altering the properties associated with the bulk of the material.

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