Biodegradable *nypafruticans* (nipa) starch-pva Biocomposite films for food packaging

Abstract

Starch-based films have been highlighted with itsbiodegradability, renewable, and amalgamation with other biopolymers as an intended substitute tosynthetic packaging. This study aims to add to the plethora of literature on advancing a novel source of starch (*Nypafruticans*) in combination with PVA and plasticizers to enhance the properties of thebiocomposite film. The film's physicochemical and food packaging properties were analyzed in terms of their water content, solubility, water vapor permeability, tensile strength, elongation at break, and transparency. The functional groups were characterized using FTIR and quantitatively analyzed the puto samples packaged in three conditions for their weight loss, sensory evaluation, and shelf life**.**The results presented the biofilm with twice the elongation at break, good light barrier property, and low water vapor permeability characteristic of a packaging's food preservation. The FTIR spectra showed the wide absorption band of the hydroxyl groups (OH) in starch and PVA and the presence of the C-O-C group representing the glucose units of starch. The food packaging analysis showed the efficiency of nipa starch biocomposite film as a prototype for a wider application in the food and packaging industry.

Keywords: Biocomposite film, polyvinyl alcohol, starch, Nypafruticans, food packaging

1. Introduction

In adapting renewable alternatives to petroleum-based packaging, biodegradable polymers were introduced as a promising resource that can eventually resolve the environmentaldesolationcaused by plasticwaste. Even further as the pandemic loomed in 2020, the threat of health issues rippled into the surge of plastic waste with the increased takeaways and deliveries [1].

Biodegradable polymers from agro-industrial wastes and byproducts are the most convenient forms of renewable polymers that areavailable in the growth cycles of every organism [2]. One of these is starch, that is heavily studied in combination with other biopolymers to improve its limiting mechanical properties. Reinforcing fillers encompass fibers, cellulose, synthetic and other biopolymers which are commonly studied in starch-based films [3]. In particular, polyvinyl alcohol, a synthetic biopolymer is most used in the packaging industry for its effectiveness in film formation, resistance to most solvents, complementing the high cost of PVA with starch's low cost, good compatibility with their strong properties and even enhancing further its biodegradability feature [4].

In the search for starch sources, *Nypafruticans*, a perennial mangrove palm tree was found to be studied by Calderon and Lim[5] as a viable source of starch in producing silver nanoparticles. Simply known as nipa, the dimorphic fruit-bearing tree [6] is utilized in Northern Samar inyielding vinegar from its young flower's sap or when fermented is produced into alcohol called tuba or sasa*.* While the leaves are made into roof and wall thatching's, baskets, or hard brooms, the potential of nipa seeds remains to be used as the focal point in future studies.

This study will synthesize a biocomposite film with extracted nipa starch from its seeds reinforced with polyvinyl alcohol and plasticized with the synergy of glycerol and sorbitol to enhance the mechanical properties and water sensitivity of starch. This research will frame a new avenue for nipa fruit to be utilized in creating environmentally favorable packaging that is also favorable for the economic well-being of citizens in Northern Samar

2. METHODOLOGY

The *Nypafruticans* (Nipa) fallen fruits were collected at Brgy. Bantayan, San Roque, Northern Samar, Philippines. The process of conventional starch extraction, development of biocomposite film, physicochemical tests, and food packaging analysis were conducted at the Technology Innovation Center, University of Eastern Philippines, University Town, Catarman, Northern Samar.

2.1 Isolation of Starch

The preparation of starch was employed based on Calderon and Lim [5] with small modifications. Nipa seeds were chopped and soaked in sodium metabisulfite solution. The seeds were then blended until paste and filtered with cheesecloth. The filtrate was soaked again with sodium metabisulfite solution and allowed to settle. The starch mucilage was washed several times with sodium metabisulfite and allowed to stand after every wash. The washed starch mucilage was dried in the dehydrator for several hours. The dried starch was then finely grounded, sieved, and kept for analysis.

2.2 Preparation of Biocomposite Film

Cui-Lim and Bangco[7] and Banda *et al.'s*[8] procedure was adopted for the preparation of biocomposite film with modifications. Nipa starch was boiled in distilled water and then filtered. The nipa starch filtrate was dispersed ina PVA solution with drops of sorbitol and glycerol to allow gelatinization until 90°C. This fixed amount of solution was cast in a glass plate and dried in an oven. The film was further dried at room temperature for a few more days with the resulting dried film peeled and stored in a desiccator at room temperature until experimentation.

2.3 Physicochemical Tests

2.3.1.Water Content (WC) and Water Solubility (WS)

Quantifying the water concentration was done using the method employed by Sun *et al.*[9] with modifications. The film sample with 3 x 3 cm dimensions was weighed for m_0, then incubated for more than 3 hours at 105°C until a constant weight (m_1) was observed.For 24 hours, the dried film (m_1) was immersed in 100 mL of water at 25°C. The drenched films were filtered, and the residue was weighed to obtain m_2. Then calculated with the formula:

$$WC(\%) = \frac{m_0 - m_1}{m_0} x\, 100$$

$$WS\ (\%) = \frac{m_1 - m_2}{m_1} x\, 100$$

2.3.2 Water Vapor Permeability (WVP)

Determination of WVP was patterned from the study of Júnior *et al*. [10] performed in triplicate through gravimetric method of analysis. Three glass vials with a 20 mm diameter permeation area were filled with calcium chloride desiccant at 0% relative humidity (RH). The biocomposite film was placed in the vial's mouth and sealed using packaging tape. The glass vials were stored in a desiccator containing water at 25°C and 100% relative humidity. The water vapor transmission rate was determined using the slope obtained from the "mass over time (s)" plot for every hour for the whole duration of 5 hours divided by the permeation area. The formula for water vapor permeability is as follows:

$$Water\ Vapor\ Permeability\ (WVP) = \frac{WVTR * e}{p_s * RH}$$

Where e is the film's average thickness, p_s is the water vapor saturation pressure at 25°C (23.756 mmHg), and RH is the relative humidity (1.00).

2.3.3Tensile Strength and Elongation at Break

Tensile strength and elongation at break were measuredusing a ShimadzuTensile TesterAGS-J Series (Industrial Technology Development Institute, Taguig City, Philippines)based on the ASTM D882 [11] method. The film samples of 110 microns thickness were cut into 25 mm strips held by air-actuated grips. Ten samples were separated by 50 mm grips and loaded with 500 N at a test speed of 500 mm per minute.

2.3.4 Transparency

Evaluating film transparency was done using a UV-Vis spectrophotometer (BSDBU-201-B, Biolab) at wavelengths ranging from 300-800 nm. The transparency of nipa starch biocomposite film and polypropylene packaging was expressed as the percent transmittance measured at 600 nm [12].

1.4 Fourier Transform Infrared Spectroscopy

An attenuated total reflection (ATR) method was used in recording the FTIR spectrum of nipa starch biocomposite films and was applied directly onto the ZNSe ATR cell with 64 consecutive scans at 500 to 4000 cm^{-1}wavelengths, this was taken from the study of Dagalea and Lim (2021) [13].

2.5 Food Packaging Analysis

2.5.1Statistical Analysis of Sensory Evaluation of *Puto*

Puto was prepared, cooked, and packed under 3 different conditions, namely with polymer biocomposite film, with polypropylene material, and unpacked. Three (3) replicates for each condition were conducted. The dry food sample was stored in a hygienic storeroom.

In the span of 7 days, observation and recording of visual quality in terms of appearance and odor was conducted each day. A panel of 5 informed persons evaluated the quality of stored *puto* using the 9-point hedonic scale, where 8-9 denotes excellent and fresh appearance, 6-7 denotes good, 4-5 denotes fair (limit of marketability), 2-3 represents fair (useable but not saleable), and 1 indicates that the product is bad and unusable [14].

The sensory evaluation of appearance and odor in three packaged forms of the *puto*samples was calculated at their resulting average for three trials. The means were calculated in the span of 7 days for each packaging condition in each sensory parameter and were expressed through analysis of variance (ANOVA) with a 0.05% level of significance.

2.5.2Weight Loss

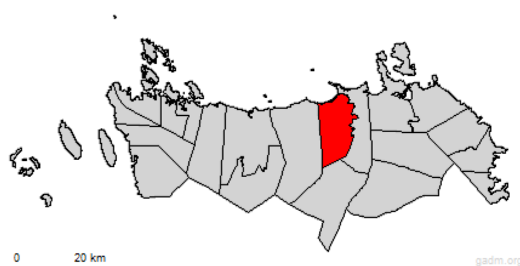
The *Puto* in its packed versions with developed biocomposite film and polypropylene packaging and unpacked version was weighed every day in the span of 7 days. The value of percent weight loss was computed according to Mohebbi *et al*. [15].

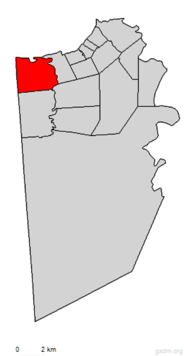
$$Weight\ Loss = \frac{W_0 - W_f}{W_0}\ x\ 100$$

Where W_0 is the weight before the degradation test and W_f stands for weight after weight loss test

2.5.3 Shelf Life

Puto was assessed visually for freshness, changes in color and odor. When the *puto* was rendered bad and unusable in any of the two parameters (1 point on the 9-point hedonic scale) due to the appearance of brown spots and molds or smelling unpleasant, the storage was discontinued [14].





Map 1. **Nypafruticans fallen fruits were collected at Brgy. Bantayan, San Roque, Northern Samar, Philippines**

3. Results and Discussion

3.1 Physicochemical Tests

Inferred from the moisture content, the developed biocomposite film revealed an average of 21.25% water molecules occupying the total structure of the filmwhich shows the compatibility of water molecules to the hydroesc structures in starch and PVA. Meanwhile, Adjouman*et al.* and Alves *et al*. observed the increase of moisture content in starch-based films being influenced by the increase in glycerol concentration. Moreover, the film's solubility in water at 100% reflects the reduced water resistance of the film and thus induces a faster biodegradation rate [16].

Conversely, a4.58× 10^{-12} ±1.92 × 10^{-12} (g/s m Pa) WVP value was calculated in comparison to low-density polyethylene's (LDPE) WVP at 6.97 × 10^{-12} ± 7.74 × 10^{-13} (g/s m Pa) [17]. It shows a smaller value that suggests a betterbarrier against water exchange with the environment and with the packaging itself. Gutierrez *et al.* [18]suggest further that hydrophilic film's WVP is positively correlated with film thickness, finding that the lower value of WVP correlated to the thinnest film produced.

Additionally, the data in Table 1 implies that the biocomposite film has a weaker ability to resist breaking under applied pressure (6 N/mm^2<40 N/mm^2) but has twice the resistance towards length deformation (elongation) than the commercial film (222%>100%) [19].This phenomenon is observed due to the hydrophilic character of the hydroxyl and other polar groups leading to swelling of the natural fibers, deterioration of the fiber matrix, plasticized effect, and expansion of fiber bundles that reduces the mechanical properties of the film[20].

As shown in Table 1, the biocomposite film exhibited lower transmittance values at an average of 29.92% in comparison to polypropylene packaging observed to have high transmittance at an average of 84.98%.Transparency is the property that is valued the most by consumers as it allows evaluation of food's freshness and appearance before purchasing. The data suggests then that the developed biocomposite film will have lesser appeal to consumers who value food packaging transparency. Nevertheless, low transparency at the visible region (200-800) suggests a good barrier against UV/visible light radiation as stated by Peralta et al. [21] light can hasten the process of food degradation and oxidation.

Table 1. Summary of physicochemical properties of Nipa starch biocomposite film

Parameters	Nipa Starch Biocomposite	Standard Packaging

	Film	
Water Content	21.25%	0.25%
Water Solubility	100%	0%
Water Vapor Permeability	$4.58 \times 10^{-12} \pm 1.92 \times 10^{-12}$ g/s m Pa	$6.97 \times 10^{-12} \pm 7.74 \times 10^{-13}$ (g/s m Pa)
Tensile Strength	6.06 N/mm^2	40 N/mm^2
Elongation at break	222.67%	100%
Transparency	29.92%	84.98%

3.2 Fourier Transform Infrared Spectroscopy (FTIR)

Figure 1, presented absorption bands of nipa starch biocomposite film at 3294 cm^{-1}reflecting an OH stretch, at 2940 cm^{-1}, and 1375 $cm^{-1}$is the C-H bands of alkyl and alkane groups, at 1712 $cm^{-1}$the carbonyl (C=O) of residual acetate groups of PVA and at 1248 cm^{-1} and 1084 $cm^{-1}$the vibration of CO and stretching of CC were defined to be C-O-C groups of the glucose unit of starch. (IR Table, UCLA)

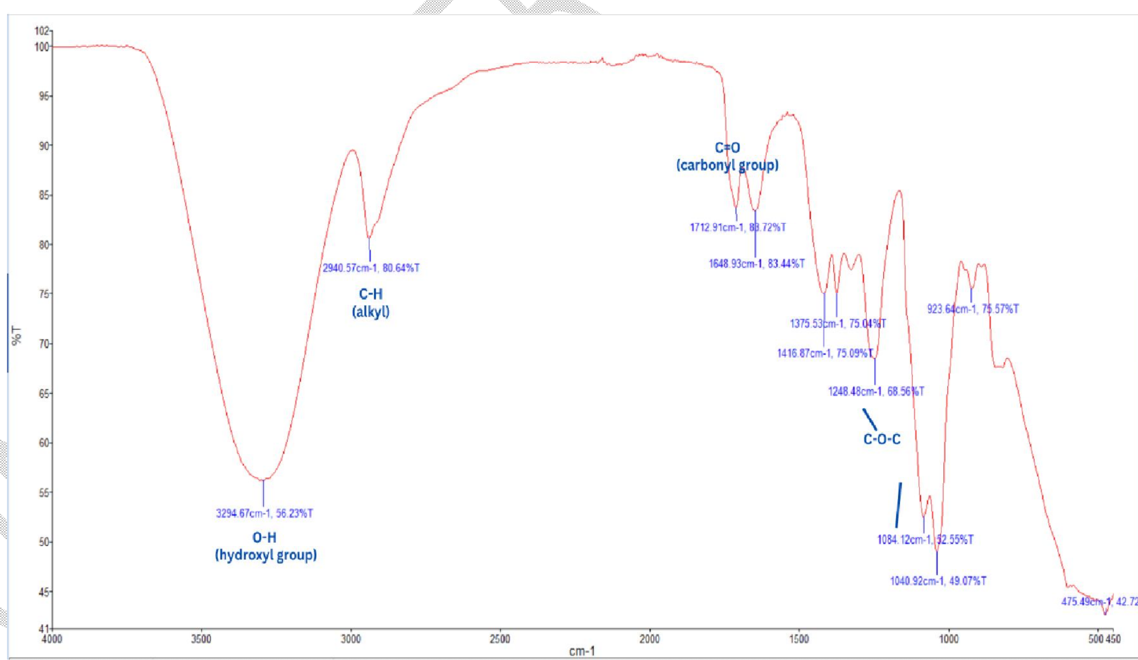


Figure 1. FTIR spectrum of nipa starch biocomposite film

3.3 Food Packaging Analysis

The P values for *puto's* appearance and odor were all greater than the significance level at p<0.05 as shown on Table 2. This accepts the null hypothesis that there is no significant difference between the performance of biocomposite film, polypropylene packaging, and unpacked versions in preserving the food samples. This further indicates that the biocomposite film is viable as a packaging alternative to the commercial sheet as it exhibits the same level of protection.

Table 3shows that polypropylene is the most effective at preserving the weight of puto while the biofilm exhibited effectiveness second to the commercial packaging. This data correlates with the findings from the physicochemical properties of the biocomposite film exhibiting a high water absorption rate thus the formulation needs further improvement.

Lastly, the shelf life of *puto* packaged with polypropylene ended on day 5 due to molds and foul smell while those sealed in biocomposite film showed no difference in its appearance until the 6th day when a less pleasant smell arose on the sample. Similarly, the unpacked version had a shelf life of 6 days when its aroma changed after.

Table 2. Analysis of Variance (ANOVA) of Sensory Evaluation of *Puto*

Sensory Parameters	F	P-value	F crit
Appearance	0.160056	0.853125	3.4668
Odor	0.060329	0.809541	4.60011

Table 3. Weight Loss and Shelf Life of *Puto* in the Span of 7 Days

Parameter	Biocomposite Film	Polypropylene Packaging	Unpacked
Weight Loss	4.71%	2.98%	5.17%
Shelf Life	6 Days	5 Days	6 Days

4. Conclusion

The study finds nipa starch biocomposite films to be an effective source of packaging alternatives. The pervasiveness of the Nipa palm tree could help acquire additional sources of starch and reduce the cumulative effect of plastic wastethus increasing the livelihood of the farmers and encouraging the cultivation of Nipa palm species and thereby improving their livelihood and business. To further enhance this study, various concentrations of nipa starch must be examined to compare its effect in exhibiting physicochemical and food packaging properties. Additional testsare needed with TGA, SEM, Colorimeter, Texture Analyzer, and X-ray Diffraction to determine the integrity of the film in food preservation and natural degradation.

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