

DEVELOPMENT OF BIODEGRADABLE PACKAGING WITH IMPROVED HYDROPHOBICITY BY USING NATURAL FIBERS BEING MODIFIED BY POLYLACTIDE AND PALMITIC ACID

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Abstract

The widespread use of single-use packaging materials, particularly food packaging, contributed to plastic waste issues. Consequently, researchers aimed to develop alternative biodegradable packaging in order to reduce plastic waste problems from conventional plastic. The alternative packaging materials were made from fibers deriving from plant weeds being formed into paper sheets and coated with a 0.4% (w/v) polylactide (PLA) and different concentrations of palmitic acids, which were compatibilized by high epoxy group chain extenders. The morphological result showed that good adhesion of the paper made of fibers from the Narrow-leaved cattail was coated with a PLA film and dispersed by micelles of palmitic acid. The FT-IR revealed the chemical interaction between PLA and cellulose fibers on the paper with the presence of epoxide-based reactive agents. The XRD results showed that the crystallinity of cellulose paper was changed when it was composite. The water absorption test, all formulations exhibiting a water absorption time exceeding 2 h, influenced by the presence of palmitic acid. The contact angles were at 125.94 ± 4.24 and 125.34 ± 4.41 degrees, respectively. Additionally, the papers maintained hydrophobic properties for over an hour.

Keywords: Biodegradable; Coating; Fatty Acid; Narrow-Leaved Cattail; Polylactide; Sustainable Food Packaging

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Introduction

The increase in single-use food packaging significantly contributes to the waste problem. This issue emphasized the need for alternative materials for replacing single-use plastic products. Polylactide (PLA) is one of the biodegradables with high potential for packaging due to its affordability, ease of processing and the glass transition temperature (T_g) of PLA which was higher than room temperature. This made it be suitable for subzero application. However, the PLA had some drawback on its properties. To overcome this limit, the biodegradable plastic modification and some applications were necessary for some performances.

One common approach for improving PLA properties involved with adding fillers for enhancing some properties according to its purpose such as thermal stabilities (Khankruea *et al.*, 2013) or dielectric properties (Triamnak, 2023). Polymer blending was another widely used technique for achieving desirable properties in biodegradable polymers. The brittleness was the weakness of PLA being blended with engineering plastic PLA/Polyamide 6 (Khankruea *et al.*, 2014) in order to toughen polymer and increase thermal stability or blended with copolymer PLA/Ethylene vinyl acetate for some application purpose such as shrink film application (Khankruea *et al.*, 2019). For fully biodegradable, packaging being blended with both phases was biodegradable. It was a challenge in order to improve some drawback and still be fully biodegradable. The reactive PLA/Polybutylene succinate (PBS) blending (Kajornprai *et al.*, 2021) was one of the most popular blending in order to improve impact properties or develop the textile applications (Boonyod *et al.*, 2023). In many applications, PLA bio-composite had a potential to improve its mechanical properties.

The cellulose fiber played the important role on improving the mechanical properties of PLA according to biodegradable, good thermal mechanical properties. PLA/cellulose fiber hybrid was composite with Talc in order to enhance their crystallization (Nanthananon *et al.*, 2018a). However, poor interfacial adhesion between PLA and cellulose fibers remained a significant challenge (Murariu and Dubois, 2016). The interfacial interaction was a major challenge.

The compatibilizer for composite material had been introduced, the multi-epoxy group chain extender as a compatibilizer between matrix phase (PLA) and dispersion phase (cellulose fiber) which could improve their morphological property which was confirmed by SEM and molou testing (Nanthananon *et al.*, 2018b). The multi-epoxy group

chain extender, Joncryl ADR-4368, compatibilized PLA/Sisal fiber was composite which enhanced interfacial interaction and increased mechanical properties (Wu and Hao, 2019).

The biodegradable material being plenty on earth, low cost and satisfactory mechanical properties was cellulose which could be derived from agricultural products being widely used in paper packaging (Liu *et al.*, 2021). However, its hydrophilic nature limited its water barrier property, which was critical for many applications. Coating cellulose-based paper had been shown that it improved water resistance properties. For example, beeswax coatings enhance water resistance (Zhang, 2014), while Chitosan coatings improved water resistant in seedling bag applications (Khamsao *et al.*, 2021). Spray coating with biodegradable polymer such as Polybutylene succinate-co-adipate (PBSA) on kraft paper was accomplished in case of improving water contact angle and water resistant (Kyaw *et al.*, 2024). Our previous work was completed in case of coating PLA on cellulose fiber from water hyacinth (Wutisart, 2020) to improve the water resistance. Yet, the interfacial adhesion was still poor. To enhance morphological properties of PLA coating on cellulose fiber from Narrow leave cattail, it incorporated with multi-epoxy group chain extender named Joncryl[®] ADR4468 as a compatibilizer of PLA/cellulose (Wutisart and Khiewbanyang, 2023) which accomplished to improve morphology and reveal the chemical interaction indicated by FT-IR spectra (Mujica-Garcia *et al.*, 2016). Nevertheless, water resistant needed to be improved.

The fatty acid was known for biodegradable polymers additives and decreased water vapor permeation (Fakhouri *et al.*, 2009). The palmitic acid was combined as PLA plasticizer for improving melt properties (Darie-Niță *et al.*, 2016). The palmitic acid could increase hydrophobicity of PLA/PBS blend being indicated by water contact angle and miscible to PLA (Ratsameetammajak *et al.*, 2018).

The objective of this work was to improve water barrier properties of cellulose paper from Narrow leaved cattail by using bio co-coating PLA and fatty acid in this study which was palmitic acid according to previous work and solid at the room temperature with the possibility that palmitic acid would turn the hydrophilic head to the cellulose which has high polarity and turn hydrophobic tail outside, which increased hydrophobicity and water endurance packaging materials. These processes

were in solution coating and varied content of palmitic acid for packaging application.

Materials and Methods

Materials

Poly(lactide (PLA), 3052D was purchased from Ingeo[®]. Narrow leaved cattail was supplied from Dhonburi Rajabhat University Samut Prakarn. The high epoxy chain extender Joncryl[®] ADR4468 as a compatibilizer in this experiment was from BASF and the fatty acid in this work was palmitic acid.

Paper Fabrication

Narrow leaved cattail stem was extracted for fiber with 5%wt of NaOH for 1 h then washed until neutral and ambient dried for 1 day. The extracted fiber was fabricated to be a paper by separating fiber in water the fiber and filling on wire mesh and hot air oven dried at 60°C for 2 h.

Solution Coating

The solution was prepared by dilute 0.4% (W/V) of PLA in dichloromethane. After the PLA fully dissolved, Joncryl[®] ADR4468 was added containing 20 ppm. In this work, we varied 2 contents of fatty acid, containing 0.1% (W/V) (designated as FA1) and 0.2 % (W/V) (designated as FA2) of fatty acid respectively (Table 1). The fabricated paper was coated by dipping in solution for 1 min in every content and ambient dried.

Characterization and Testing

Morphological Investigation

The surface and cross sectional of paper composite was investigated by Scanning Electron

Microscope (SEM) (TESCAN MIRA3 LMH Schottky, Brno, Czech Republic), the sample was coated with a thin layer of gold.

Functional group Characterization

The chemical interaction of the paper composite was confirmed by Fourier Transform Infrared (FT-IR) Spectroscopy. The sample were characterized by Perkin Elmer FT-IR Spectrometer.

X-ray Diffraction

The XRD analysis of the paper composite was performed using Malvern Panalytical, Aeris at the starting and ending position of 2θ at 5.0054° and 79.9924° respectively.

Contact Angle and Water Absorption

The water contact angle in this study was performed for the application of food packaging. To show the water resistance, the change of water contact angle was continuously recorded by the time over 2 h at least 7 samples which were tested at the room temperature.

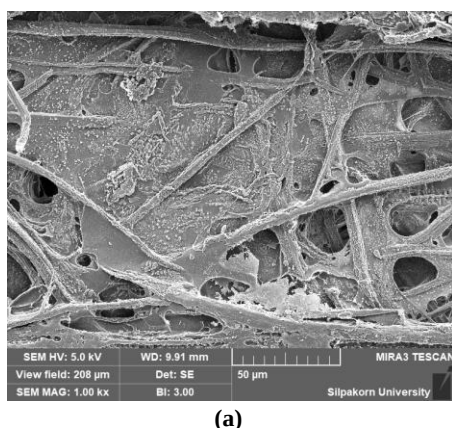
Table 1. List of composition

Formula	PLA (%w/v)	Joncryl [®] ADR4468 (ppm)	Palmitic acid (%w/v)
Neat Paper	-	-	-
FA1	0.4	20	0.1
FA2	0.4	20	0.2

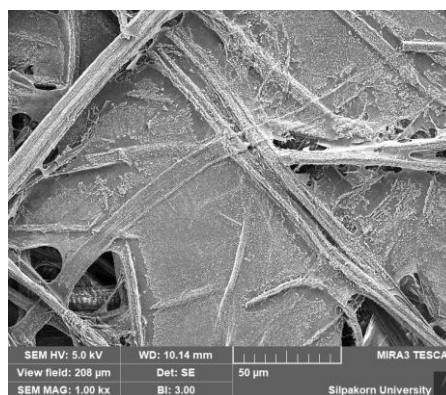
Results and Discussion

Morphology

The morphology of Narrowed-leaved cattail paper from Narrow leaved cattail with PLA and



(a)



(b)

Figure 1. SEM Image on surface of FA1 (a) and FA2 (b) at 1000X

Fatty acid coating was carried out by SEM imaging on both surface and cross section to investigate the presence, shape, size and phase adhesion of composites.

As shown in Figures 1(a) and 1(b), both FA1 and FA2 showed the PLA thin film coating on the surface (Wutisart, 2020). It showed the good adhesion between surface of cellulose from Narrow leaved cattail and PLA being affected by multifunctional epoxy group of compatibilizer (Wutisart and Khiewbanyang, 2023). It found out small particles of palmitic acid on both FA1 and FA2.

As seen on the higher magnitude (30,000X), the palmitic acid agglomerating on the PLA film in submicron size and treating as the plasticizer of PLA which could miscible to PLA being confirmed by a former reported (Ratsameetammajak *et al.*, 2018). SEM images showed the good adhesion on the surface (Figures 2(a) and 2(b)). The FA2 had the same size and good adhesion of palmitic acid

particle. Nevertheless, FA2 showed the higher presence of palmitic acid particle according to higher content of palmitic acid.

The cross-section image confirmed a good adhesion between palmitic acid and PLA film showing that the palmitic acid particle was not pulled out from the PLA film (Figure 3(a)) when the paper deformed. The same result of FA2 (Figure 3(b)) was with a higher presence of palmitic acid particle.

Functional Group Characterization

The chemical interaction between composites needed to be confirmed by functional group analysis. The reaction of composites with compatibilizer comparing with Neat fiber was characterized by FT-IR spectra. From Figure 4 the peak was located at $1,756\text{ cm}^{-1}$ on both FA1 and FA2 indicating to the carbonyl group (-C=O) stretching of the ester group of PLA. This was confirmed about the reaction between PLA and cellulose fiber

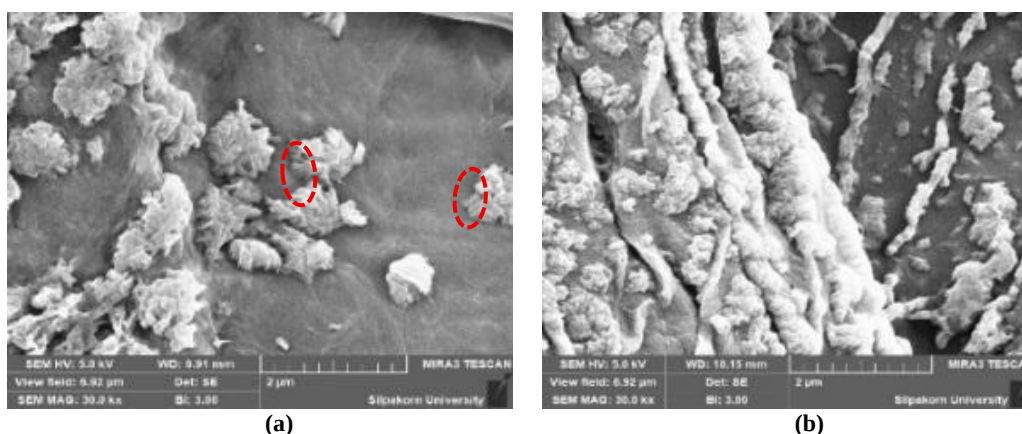


Figure 2. SEM Image on surface at 30000X of FA1 (a) and FA2 (b)

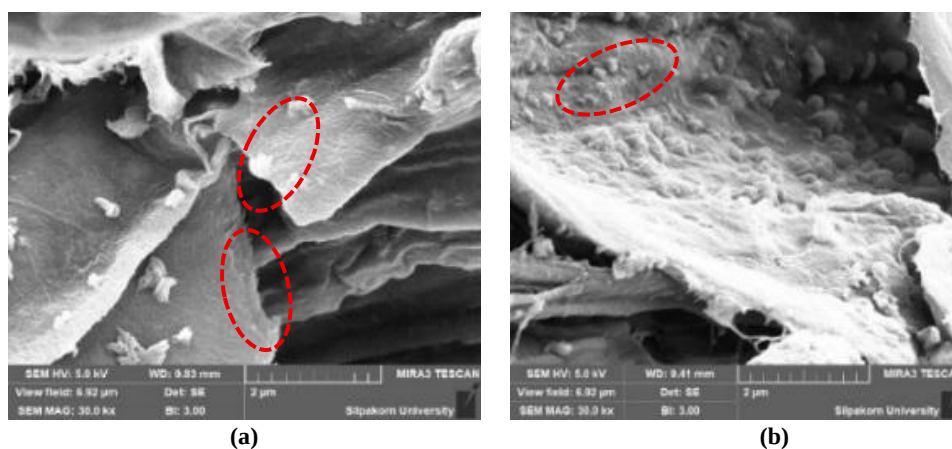


Figure 3. SEM Image on cross section at 30000X of FA1 (a) and FA2 (b)

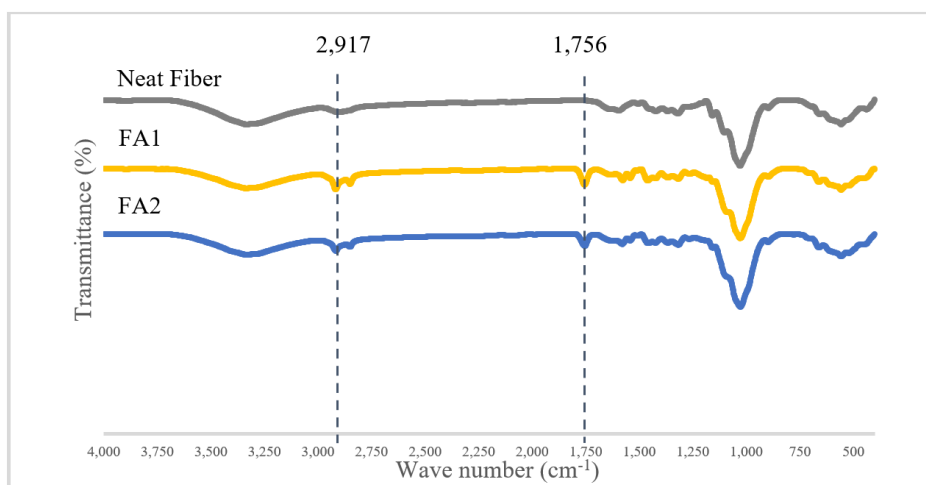


Figure 4. FT-IR Spectra of Neat narrow leaved cattail fiber, FA1 and FA2

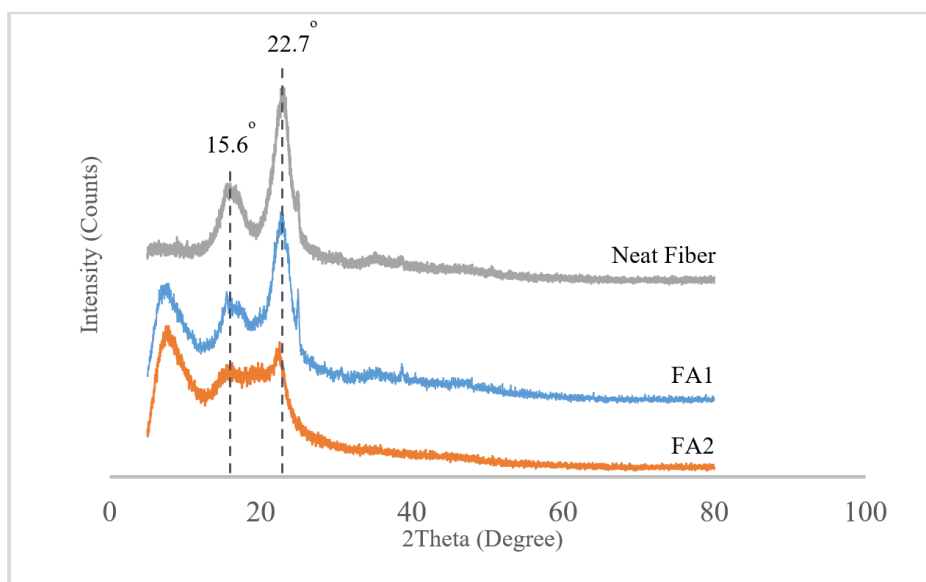


Figure 5. X-ray Diffraction

by grafting procedure (Mujica-Garcia *et al.*, 2016). On the other hand, the multifunctional chain extender could be utilized in solution coating (Wutisart and Khiewbanyang, 2023). And also, the peak located at $2,917\text{ cm}^{-1}$ on both FA1 and FA2 which was assigned C-H stretching according to palmitic acid exhibiting on composite.

X-ray Diffraction

The XRD pattern (Figure 5) of Neat fiber presented 99 series of peaks corresponding to cellulose peak pattern with 2 theta of 15.6° and 22.7° . Both FA1 and FA2 showed broad peak of PLA and indicated that composites were flatten the peak at 15.6° and 22.7° , especially in FA2 with

higher content of palmitic acid. This referred to the composite preferentially adhered to specific cellulose crystal planes, reducing the intensity of cellulose-specific diffraction peaks.

Water Contact Angle and Absorption

For the packaging, especially in frozen product, water barrier properties needed to be tested. Firstly, the water contact angle was measured then recorded the water contact angle changing in every 10 min. The test revealed the water contact angle from the start of FA1 and FA2 were $125.94 \pm 4.24^\circ$ and $125.34 \pm 4.41^\circ$ (Figure 6) respectively. These showed that the hydrophobic surface from the roughness of paper increased water resistant

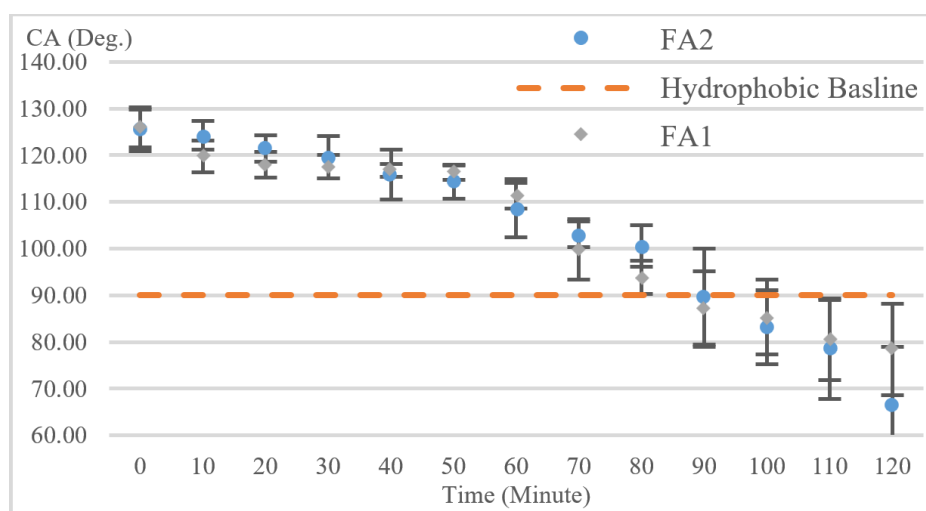


Figure 6. The change of Water Contact angle on FA1 and FA2

from PLA film. There was the possibility that fatty acid turned the hydrophobic tail out of the paper in both FA1 and FA2. The record of water contact angle change was still hydrophobic until 80 min from the start and became hydrophilic at 90 min. To compare with single PLA coated on paper (Wutisart and Khiewbanyang, 2023), this showed the increasing water resistant from palmitic acid. The water contact angle remained recorded until 120 min and the water was not fully absorbed. This was almost 5 times longer than our former work and confirmed that this material had the water resistant for the frozen fish package. From the error bar, the water resistant of FA1 and FA2 was not significantly different, this implied that the low content of palmitic acid could increase water resistant of paper.

Conclusions

The PLA and palmitic acid being composite on the paper from Narrow leaved cattail revealed the good adhesion on the composite with multifunctional epoxy group chain extender. The PLA film PLA covered on the surface of paper without penetration inside the fiber and palmitic acid agglomerated in submicron size particle on both FA1 and FA2. This adhesion was confirmed by functional group characterization from FT-IR spectra which indicated the carbonyl group stretching and C-H stretching. This verified the chemical interaction on composites which were consisted of ester group and alkane from PLA and palmitic acid respectively. The XRD presented

the flatten peak of cellulose crystal corresponding to the higher content of palmitic acid. Both FA1 and FA2 exhibited the hydrophobic surface being tested by water contact angle measurement. This test remained hydrophobic for 80 min and could resist water more than 2 h.

FA1 and FA2 had good properties for frozen fish packaging development. Nevertheless, FA1 (PLA 0.4%(w/v), ADR4468 20 ppm and palmitic acid 0.1%(w/v)) added lower content of palmitic acid with satisfactory result. This was an advantage for industrial level on cost saving on manufacturing in the future. The next step of our study was PLA film laminate composite and testing in the real frozen fish product. This work presented the paper from Narrow leaved cattail composites with PLA and palmitic acid in solution coating had potential for developing the frozen fish package by costing effective application and biodegradable materials.

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