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Development of Green Leather Alternative from Natural Rubber and Pineapple Leaf Fiber

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Abstract: In the present research, a plant-based leather substitute material or leather alternative was developed from natural rubber (NR) and pineapple leaf fiber (PALF) using a simple process. Pineapple leaf fiber was extracted from waste pineapple leaves using a mechanical method. Untreated PALF (UPALF) and sodium hydroxide-treated PALF (TPALF) were then formed into non-woven sheets using a paper making process. PALF non-woven sheets were then coated with compounded natural rubber latex at three different NR/PALF ratios, i.e., 60/40, 50/50, and 40/60. Epoxidized natural rubber with an epoxidation level of 10% (ENR) was used as an adhesion promoter, and its content was varied at 5, 10, and 15% by weight of the total rubber. The obtained leathers were characterized in terms of tensile properties, tear strength, and hardness. The internal structure of the leathers was observed with a scanning electron microscope. Comparison of these properties was made against those reported in the literature. It was found that the leather with NR/PALF equal to 50/50 was the most satisfactory; that prepared from TPALF was softer and had greater extension at break. With the addition of ENR at 5%, the stress-strain curve of each respective leather increased significantly, and as the amount of ENR was increased to 10 and 15%, the stresses at corresponding strains dropped to lower values but remained higher than that without ENR. PALF leather prepared in this study has comparable or better properties than other alternative leathers reported in the literature and is much stronger than that made from mushrooms. Thus, this type of leather alternative offers unique characteristics of being bio-based and having a lower carbon footprint.

Keywords: natural rubber; non-woven fiber sheet; pineapple leaf fiber; leather

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1. Introduction

The world is now facing a number of problems relating to climate change, resources, and the environment that result from past unsustainability. Thus, a circular economy, in which materials are reused and kept in product cycles as long as possible before being considered waste, has become a necessity. In addition, a bioeconomy, in which renewable biogenic raw materials are used instead of fossil fuels or petroleum to manufacture different kinds of products, would lead to a more sustainable world. These have caused a number of changes to different industries, including the leather industry [1]. Although leather is a bio-based material, there has been a great deal of effort to find alternative materials since the beginning of the industrial revolution, for various reasons depending on the period considered [2]. Leather alternatives are also known as artificial leather, synthetic leather, and faux leather. A good introduction to the history of leather alternative materials

may be found in Meyer et al. [3] and references cited therein. For the current period, the most important reason is sustainability. Again, a new type of leather alternative, derived from food or industrial wastes, has captured the public attention via social media and the literature. Developments of leather alternatives may fall into the following categories [3]: 1. fibrous materials produced by microorganisms [4–6]; 2. replacing parts of synthetic coating materials (polyvinyl chloride (PVC) or polyurethane (PU)) with agricultural waste or plant-based materials [7–9]; and 3. coating a renewable, non-woven support with bio-based polymers [10,11]. Examples of these leather alternatives that have appeared in the media are Appleskin, which is made from apple scraps left over from the juicer process [12,13]; Desserto, made from dried cactus pulp [14]; Pinatex, made from pineapple leaves [15,16]; and Muskin, made from mushrooms [17]. Properties of these leather alternatives can be imagined to vary greatly depending on the structure of the material itself [3]. For example, Saha et al. [18] showed that artificial leather can be prepared from the pulp of kombucha, maple leaves, and apples together with polyvinyl alcohol, polycaprolactone, polylactic acid, and glycerol. However, the leather's tensile strength and tear resistance are relatively low, three times lower than that of polyurethane (tensile strength ~5.3 MPa and tear strength ~79.2 N/mm). Therefore, this may be a limitation in the actual use of the products. Bustillos et al. [19] examined the chemical composition and the mechanical, thermal, and antibacterial properties of biodegradable mushroom skin, or MuSkin. Due to the natural constituents of mycelium, this mushroom leather has antifungal and antibacterial properties. However, this artificial leather has relatively low mechanical properties (tensile strength ~572.5 kPa (0.6 MPa) and modulus ~1.2 MPa) compared with other leather alternatives on the market [3]. The main limitation of this type of artificial leather is its relatively low mechanical properties; it thus requires the use of reinforcement or support materials commonly used in commercial artificial leather. Although different combinations of natural materials and natural fibers have been invented to form leather alternatives, parts of those combinations still needed to be explicitly grown or cultivated, which requires arable land, water, and fertilizer [10]. Therefore, choosing to use natural agricultural waste materials that do not need to be cultivated is a very interesting option.

Previous studies have demonstrated the utilization of pineapple leaf fibers (PALF) derived from agricultural waste as reinforcing materials in both plastics [20–23] and rubbers [24–26] to enhance the mechanical properties of these materials. Therefore, utilizing pineapple fibers as a supporting material for flexible rubber or latex to create a leather-like appearance represents an intriguing and sustainable approach to producing a 100% bio-based leather alternative. Consequently, this research aims to explore the production of a leather alternative from pineapple leaf fibers and natural rubber. The investigation includes an examination of the effects of fiber surface treatments and the use of epoxidized natural rubber (ENR) as an adhesion promoter between the rubber matrix and PALF on the mechanical properties, thermal properties, and morphological characteristics of both the fibers and the resulting leather.

2. Materials and Methods

2.1. Materials

High-ammonia natural rubber latex (NR) with a density of 0.94 g/cm^3 was supplied by Thai Rubber Latex Corporation (Thailand) Public Co., Ltd. (Bangkok, Thailand). Epoxidized natural rubber (ENR) with 16% dry rubber content (DRC) containing 10 mol% epoxide content was synthesized in the lab according to previous research [27] with slight modification. The curing additives used in the rubber formulation, i.e., sulfur, zinc diethyl dithiocarbamate (ZDEC), zinc oxide (ZnO), and CPL antioxidant, were purchased from Thanodom trading Thailand Ltd. (Bangkok, Thailand). Pineapple leaf fiber (PALF) was collected from cultivation areas in Bang Yang District, Phitsanulok Province, Thailand. Analytical grade sodium hydroxide (NaOH) was provided by RCI Labscan (Bangkok, Thailand). The real leather (cowhide) and PU leather used for comparing mechanical properties were sourced from the local leather industry in Bangkok, Thailand.

2.2. Natural Rubber Latex Compound Preparation

The latex compound was prepared according to the formulation shown in Table 1. In addition, 5, 10, and 15% ENR (based on total rubber) was used as a compatibilizer to improve the compatibility between the rubber and fibers, where the 6 phr of nonionic surfactant was required to prevent latex coagulation after ENR was added.

Table 1. Formulation of NR compound.

Ingredients	Amount (phr *)
NR latex (10% DRC)	100
Sulfur	1.2
ZDEC	1.5
ZnO	0.5
CPL	1.0

* Part per hundred parts of rubber by weight.

2.3. Fiber Preparation

First, fresh pineapple leaves were collected from a plantation. The leaves were then cleaned and cut across their length into short pieces 6 mm wide. These chopped leaves were then ground and dried. The whole ground leaves (WGL) were ground and sieved to separate the non-fibrous material (NFM) from the PALF fibers. The fiber extraction process was carried out according to previous research [20,22]. The obtained PALF was then treated with a 10% NaOH solution for 1 h at room temperature. The ratio of PALF to NaOH solution was 1 g/30 mL. After treatment, the fiber was repeatedly washed with water until reaching a pH of approximately 6–7 and dried in a hot-air oven. This fiber is coded as TPALF, while the starting untreated PALF is UPALF.

2.4. Preparation of Non-Woven Fiber Sheets

The UPALF and TPALF were transformed into non-woven fiber sheets using a paper-making technique. The fibers were dispersed in water and subsequently shaped into non-woven fiber sheets using a silk screen. These sheets were then dried in a hot-air oven at 70 °C for 24 h to obtain the non-woven fiber sheets. The resulting non-woven fiber sheets have an approximate weight of 240 g/m^2.

2.5. Preparation of PALF Leather

The process for creating the PALF leather sheets commenced by pouring a predetermined quantity of NR compound into a plastic mold. Subsequently, non-woven fiber sheets were placed inside the mold, ensuring complete coverage. The composite was then subjected to drying at 70 °C for 24 h. Following the drying process, the material was removed from the mold and compressed using a compression machine, resulting in an artificial leather sheet made from pineapple leaf fibers (PALF leather). The study investigated various weight ratios of NR to PALF, including 60/40, 50/50, and 40/60. For some samples, natural coloring substances such as ground carrot, spent Thai red tea powders, and spent coffee grounds obtained from local coffee shops near the university were mixed with the NR compound before pouring into the mold.

2.6. Characterization

2.6.1. Fiber Chemical Composition Analysis

The chemical composition of the UPALF and TPALF fibers, including cellulose, holocellulose, acid-soluble lignin, and acid-insoluble lignin, was determined using standard methods [28–31] by the Industrial Services section of the Department of Forest Products, Faculty of Forestry, Kasetsart University, Bangkok, Thailand. Holocellulose is a component comprising both cellulose and hemicellulose.

2.6.2. Fourier-Transform Infrared Spectroscopy (FTIR) Analysis

Surface chemical composition analysis of the UPALF and TPALF fibers was performed using Fourier-transform infrared spectroscopy in attenuated total reflectance mode (ATR-FTIR) with a Frontier instrument from PerkinElmer, Waltham, MA, USA. Spectra were scanned over the range of 4000 cm^{-1} to 400 cm^{-1} with a resolution of 4 cm^{-1}, and each spectrum represented an average of 16 scans.

2.6.3. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was conducted using a NETZSCH (TG 209F1 Libra, Selb, Germany). The samples underwent heating from 25 °C to 800 °C at a heating rate of 20 °C/min under a nitrogen atmosphere.

2.6.4. Morphological Properties Analysis

The morphological properties of the non-woven fiber sheets and the cross-sectional morphology of the PALF leather were observed using a scanning electron microscope (JSM-IT500, JEOL, Tokyo, Japan) with an accelerating voltage of 10 kV. Samples were affixed with carbon tape and coated with a thin layer of platinum before observation.

2.6.5. Mechanical Properties Analysis

The tensile and tear resistance properties of the PALF leather were determined using a universal testing machine (Instron 5566, Instron, High Wycombe, UK) at a crosshead speed of 100 mm/min with a 1 kN load cell. Sample preparation followed ISO 3376 standards for tensile testing [32] and ASTM D624 die C for tear strength testing. Each set was tested with five tensile and tear test specimens.

2.6.6. Color Measurement

The color of different PALF leathers was measured using a color measurement spectrophotometer (UltraScan Pro, HunterLab, Virginia, USA). Each set included five samples for the examination. The lightness and color were reported as L*, a*, and b* values, where L* values range from 0 (black) to 100 (white); a* values range from −10 (greenness) to 10 (redness); and b* values range from −40 (blueness) to 40 (yellowness).

3. Results

3.1. Fiber and Non-Woven Sheet Characteristics

Table 2 shows the chemical composition of the UPALF and TPALF, where the holocellulose content is the total polysaccharide content (cellulose and hemicellulose). After treatment with a NaOH solution, the cellulose content increased from 57.19% to 88.73%, while that of hemicellulose and lignin decreased significantly, consistent with previously reported data [33,34]. These results show that the alkaline treatment can remove impurities and binders, such as hemicellulose and lignin on the surface of the PALF fiber; this was confirmed by the FTIR and SEM results.

Table 2. Chemical composition of UPALF and TPALF.

Chemical Constituent (%)	UPALF	TPALF
Cellulose (%)	57.19	88.73
Holocellulose (%)	85.49	95.37
Lignin (acid soluble)	2.61	0.87
Lignin (acid insoluble)	7.82	3.99

Figure 1 shows the FTIR spectra of the UPALF and TPALF. The characteristic peaks of UPALF at 1731 cm^{-1} and 1244 cm^{-1} are associated with C=O stretching of the hemicellulose or ester linkage of the carboxyl group in the hemicellulose or lignin and with C-O stretching of the lignin, respectively [35,36]. These peaks disappeared after the fiber was treated with

the NaOH solution. These results indicate that most of the hemicellulose and lignin were removed after the alkaline treatment, similar to that reported in previous studies [20,37].

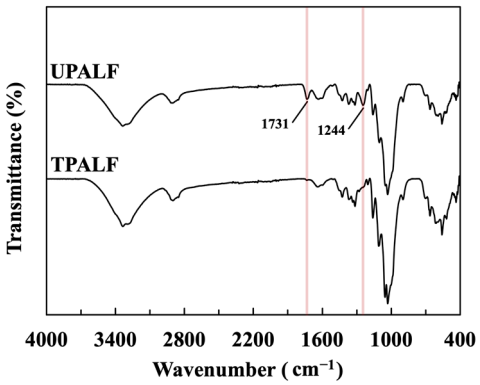

Figure 1. ATR-FTIR spectra of UPALF and TPALF.

Figure 2 shows the morphology of the UPALF and TPALF and their respective non-woven sheets. UPALF shows a rough surface due to impurities that may be hemicellulose, lignin, and wax on the fiber surface, as shown in Figure 2a. On the other hand, after alkaline treatment, the surface of TPALF shows a cleaner and smoother surface, as shown in Figure 2b, consistent with the fiber chemical composition and FTIR results.

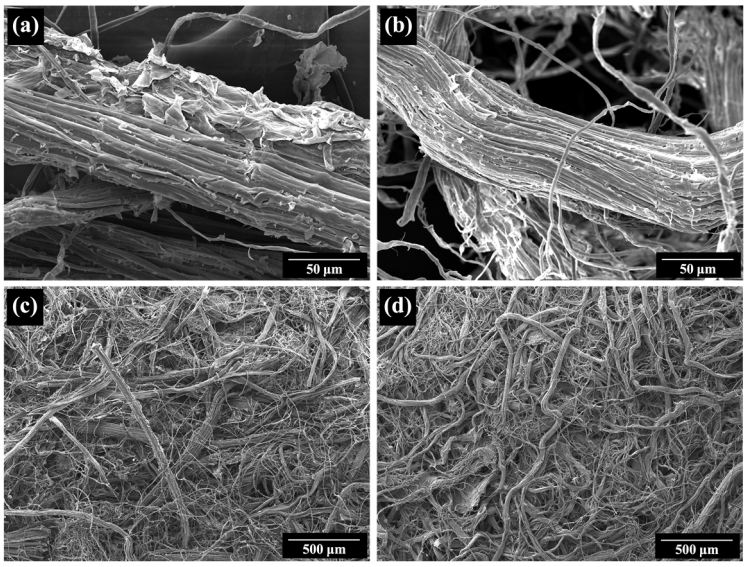

Figure 2. SEM micrographs of UPALF (**a**), TPALF (**b**), and non-woven sheets of UPALF (**c**) and TPALF (**d**).

When the UPALF and TPALF were formed into non-woven sheets, a slight difference could be observed. Non-woven sheets of UPALF are characterized by irregularly overlapping and entangled fibers, as shown in Figure 2c. Non-woven sheets of TPALF show a more entangled, smoother, and softer non-woven sheet, as shown in Figure 2d. No protruding ends of fibers are seen in the case of the TPALF sheet compared with the UPALF.

The thermal stability of UPALF and TPALF was assessed using thermogravimetric analysis (TGA). The thermograms and derivative thermograms (DTGs) for UPALF and TPALF are presented in Figure 3. Both samples exhibit two primary stages of weight loss. The first stage occurs within the temperature range of 30–150 °C, attributed to the evaporation of water or moisture content within the fibers. The second stage, observed at approximately 200–500 °C, marks the thermal decomposition of the material. This decomposition is consistent with the reported decomposition temperatures of cellulose, hemicellulose, and lignin [38].

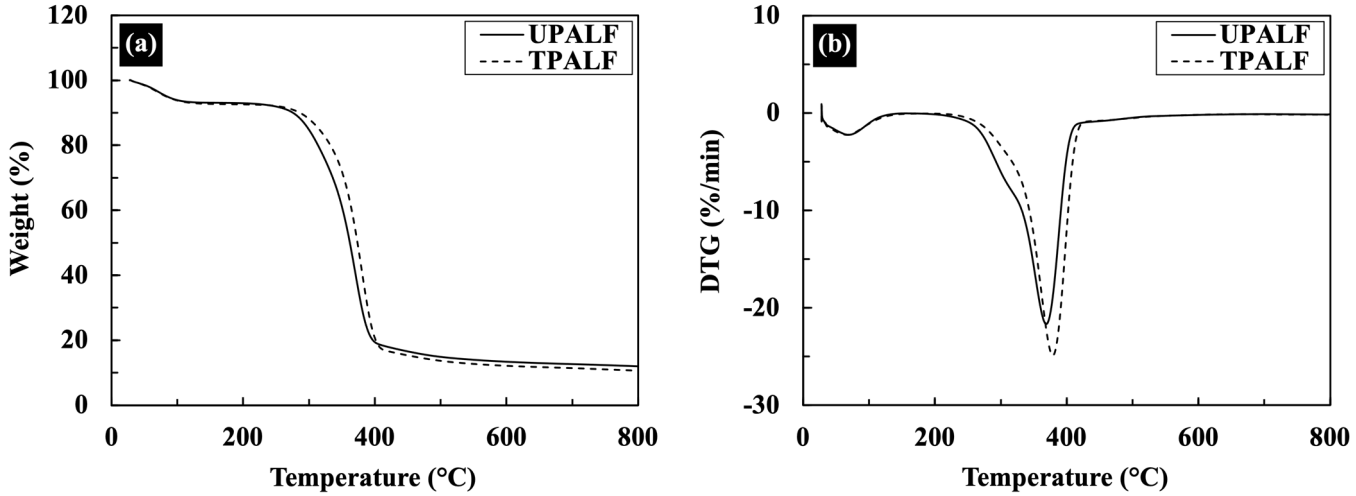

Figure 3. TGA (**a**) and DTG (**b**) thermograms of UPALF and TPALF.

It is noteworthy that TPALF's TGA curve displays a slightly higher second-stage decomposition temperature compared with UPALF. This difference can be attributed to the lower lignin content in TPALF, which is known to be less stable than cellulose. As a result, TPALF exhibits higher thermal stability compared with UPALF. Additionally, TPALF demonstrates a slightly lower percentage of residue compared with UPALF, primarily due to its lower lignin content. These findings align with previous research reports [36,39].

3.2. Mechanical Properties

The influence of PALF content on the tensile properties of PALF leather is illustrated in Figure 4. The tensile strengths of PALF leather crafted from UPALF with NR/PALF ratios of 60/40, 50/50, and 40/60 were 3.24, 4.26, and 7.13 MPa, respectively. Similarly, PALF leather created from TPALF with the same NR/PALF ratio displayed tensile strengths of 2.95, 3.64, and 6.14 MPa, respectively. The observed trend indicates that as the PALF content increases, the tensile strength of both UPALF and TPALF leather tends to increase, as the PALF fibers serve as reinforcement within this system.

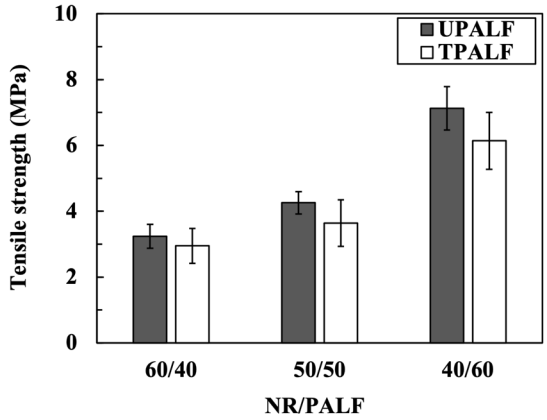

Figure 4. Tensile strength of PALF leathers prepared with different NR/PALF ratios.

The observed decrease in the strength of the TPALF leather compared with the UPALF one is rather unexpected and intriguing. After NaOH treatment, TPALF exhibits structural changes characterized by increased fibrillation, leading to the formation of finer and more flexible fibers that tend to curl. In contrast, untreated UPALF possesses larger, straight fiber bundles. This structural transformation suggests a potential increase in deformability under load for TPALF, which could impact its overall strength. While these observations provide valuable insights, a comprehensive understanding of these changes necessitates further

in-depth studies. The exact mechanisms behind the alterations in mechanical properties due to NaOH treatment require detailed exploration to unravel the complexities of these structural modifications.

However, achieving high mechanical properties is not the sole objective in the development of artificial leather, as will become clearer in a later section when we compare with commercial alternatives. Texture and the tactile experience are equally crucial factors, which can be more challenging to quantify based on individual preferences. Initially, PALF leather with an NR/PALF ratio of 40/60 exhibited impressive mechanical properties but displayed notable rigidity, akin to paper, due to the relatively high fiber content. Conversely, at an NR/PALF ratio of 60/40, it exhibited a pronounced rubbery texture. At a ratio of 50/50, the material struck a balance between rubbery and fibrous characteristics, offering moderate mechanical properties that bridge the gap between the two ratios. As a result, the NR/PALF ratio of 50/50 was selected as the baseline composition for artificial leather preparation. Subsequent sections delve into the effects of fiber surface treatment and the addition of ENR on the material's properties.

It should be noted that the selection of the 50/50 rubber:PALF ratio is based entirely on the tactile qualities, which could be considered rather subjective. Our material selection was guided by a holistic approach, considering both quantitative data and qualitative tactile qualities, ensuring a comprehensive evaluation of the PALF leather. While mechanical properties may be crucial for understanding material behavior, they may not directly reflect the tactile qualities experienced upon touch. The subjective evaluations considered during our material selection process encompassed a broader sensory assessment, including texture and rigidity, which may not be entirely captured by mechanical measurements. Therefore, our approach in selecting the 50/50 ratio was aimed at achieving a balance between paper-like and rubbery textures, ensuring that PALF leather exhibits versatile tactile qualities suitable for various applications.

The stress-strain curves of PALF leather prepared from UPALF and TPALF, utilizing a fixed NR/PALF ratio of 50/50 and varying amounts of ENR, are presented in Figure 5. These curves illustrate the combined effects of fiber surface treatment and ENR addition in enhancing the compatibility between NR and PALF. Furthermore, Figure 6 provides insights into the variations in tensile strength and tensile modulus observed in the UPALF and TPALF leathers as ENR content varies.

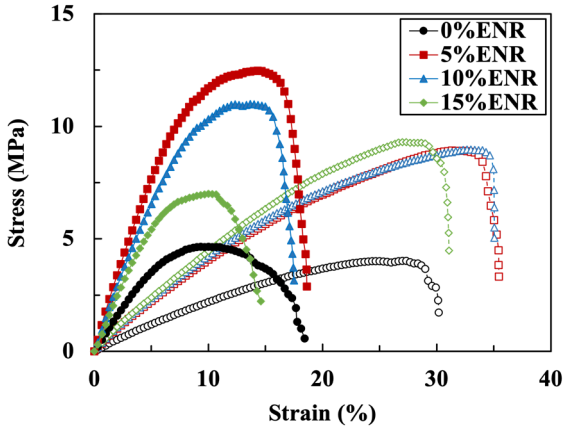

Figure 5. Tensile stress-strain curves of UPALF leather (closed symbols) and TPALF leather (open symbols) containing different amounts of ENR. NR/PALF ratio was kept at 50/50.

The tensile strength of UPALF leather at varying ENR content levels of 0%, 5%, 10%, and 15% was measured at 4.26 MPa, 12.26 MPa, 9.59 MPa, and 6.85 MPa, respectively. In contrast, TPALF leather exhibited tensile strengths of 3.64 MPa, 8.66 MPa, 8.55 MPa, and 8.53 MPa at the same ENR content levels. Meanwhile, the tensile modulus of UPALF leather at these ENR content levels measured 84.00 MPa, 193.30 MPa, 157.73 MPa, and

142.64 MPa, respectively. For TPALF leather, the corresponding tensile modulus values were 22.40 MPa, 43.21 MPa, 46.72 MPa, and 51.09 MPa, respectively.

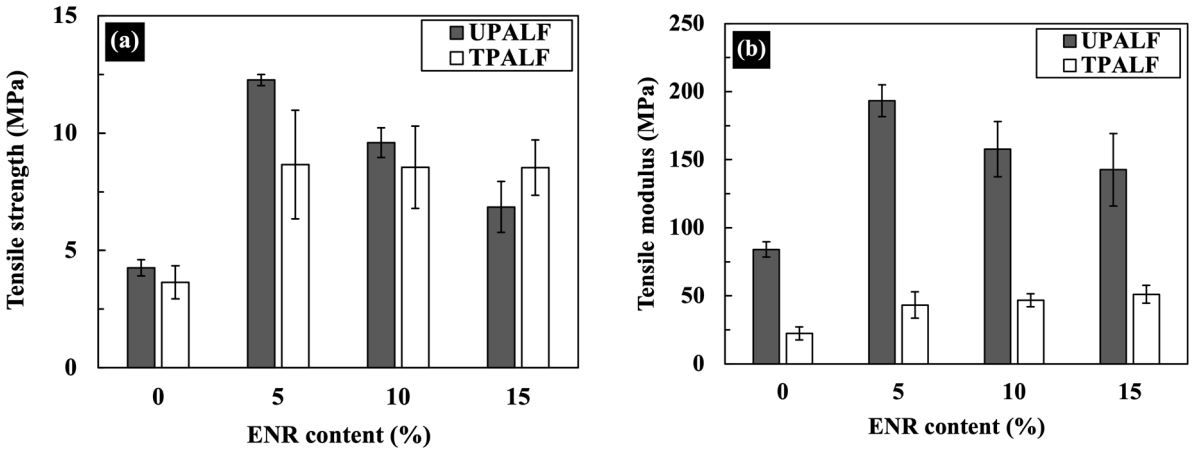

Figure 6. Tensile strength (**a**) and tensile modulus (**b**) of UPALF and TPALF leathers containing different amounts of ENR.

In UPALF leather, the addition of ENR led to an increase in tensile strength and modulus, attributed to improved compatibility and adhesion between the rubber and fibers, as observed in studies involving rubber–silica and rubber–cellulose nanocrystals [40–43]. However, beyond 5% ENR content, there was a tendency for tensile strength, modulus, and elongation to decrease. This decrease may result from a reduction in molecular weight with increasing ENR content, as ENR possesses a lower molecular weight compared with NR [44].

Conversely, when TPALF fibers were treated with a NaOH solution, tensile strength and modulus decreased, while elongation increased. This was due to the fibers becoming cleaner and softer after alkaline treatment, resulting in improved rubber–fiber compatibility. Consequently, the TPALF leather exhibited greater flexibility and elongation compared with PALF leather without alkaline treatment. Notably, the incorporation of ENR into the TPALF system did not significantly improve its tensile strength and modulus beyond 5% ENR, as the rubber–fiber compatibility had already been effectively enhanced. These findings will be corroborated with SEM micrographs in subsequent section.

Tear resistance results, shown in Figure 7a, mirrored the trends observed in the tensile properties. UPALF leather tear strength ranged from 42.17 MPa (0% ENR) to 56.70 MPa (5% ENR), with a subsequent decline at higher ENR levels. Similarly, TPALF leather exhibited tear strength values ranging from 28.18 MPa (0% ENR) to 76.03 MPa (5% ENR), followed by a decrease. The more entangled and softer TPALF fiber sheet significantly improved the tear resistance of the PALF leather.

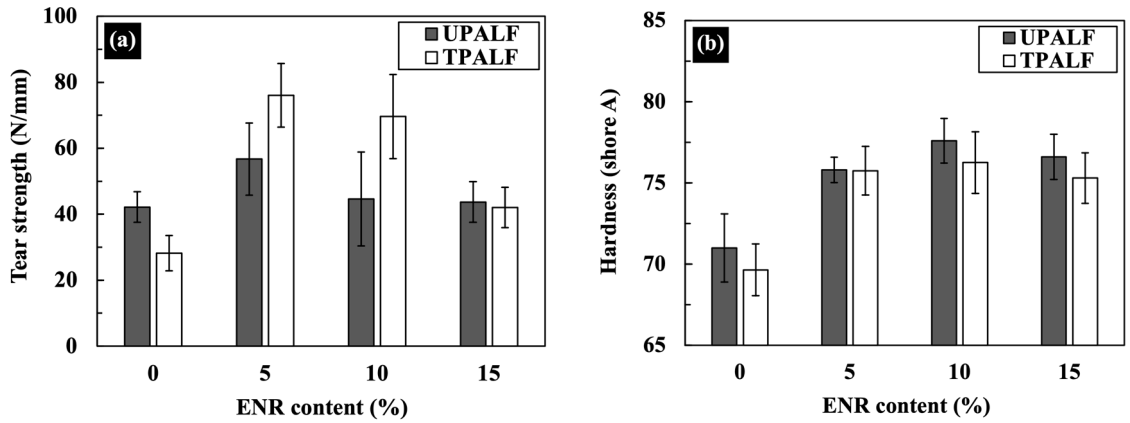

Figure 7. Tear strength (**a**) and hardness (**b**) of UPALF and TPALF leathers containing different amounts of ENR.

Figure 7b illustrates the hardness of UPALF and TPALF leathers containing varying ENR amounts. The results indicate that hardness increased with the addition of ENR, likely due to enhanced rubber–fiber compatibility, resulting in greater rigidity in line with the non-woven fiber properties.

We now assess the properties of PALF leather in comparison with other alternatives reported in the literature. Due to the wide variation in base materials, leather structure, and measurement methods across different studies, direct comparisons can be challenging. Therefore, we rely on the comparative results available in the literature. For instance, when considering alternative materials like bacterial cellulose bio-leather reinforced with plant-based protein, our PALF leathers demonstrate either similar or superior tensile strength, depending on the specific formulations (~0.5–13.0 MPa). Notably, they consistently exhibit higher tensile strength than cowhide leather (~9.3 MPa) [45]. Furthermore, when evaluating PALF leather against fungal textile alternatives prepared under various conditions (tensile strength ~2.72–19.9 MPa and elongation at break ~2–17%) [6], our materials consistently show higher tensile strength and elongation. When compared with materials with similar characteristics, such as alternative leather prepared from polyvinyl alcohol (PVA) and non-woven jute fiber sheets, it becomes evident that the fiber content in these materials is closely matched, at approximately 50% [46]. In this study, alternative leather exhibits tensile strength values of approximately 5.4 and 10.4 MPa for material thicknesses of 1.2 and 2.0 mm, respectively. It also demonstrates tear strengths of around 34.6 and 50.0 N/mm for the corresponding thicknesses. Our PALF leather, with a thickness of approximately 0.8 mm, possesses significantly superior mechanical properties. In addition, PALF leather is entirely derived from natural materials. Of particular interest in the PVA–jute study is the observation that mechanical properties tend to decrease as the fiber content increases due to an insufficient matrix. However, PALF leather exhibits a contrary trend of increasing mechanical properties. Furthermore, when compared with alternative leather prepared from natural rubber and non-woven ramie fiber with similar fiber content [10], our PALF leather also exhibits higher tensile strength properties, with a clear advantage (tensile strengths of this natural rubber–ramie fiber leather were in the range of ~1.0–5.5 MPa, depending on the condition). This is especially evident in cases where ENR is added to the mix. However, the tear strength in the natural rubber–ramie fiber leather is significantly greater than that of PALF leather, possibly due to the longer fibers and the use of a needle punch process that results in a higher interlocking of the fibers compared with the papermaking process used in the present study. This makes the leather less pliable than PALF leather produced using our method. Thus, PALF leather is well suited for a wider range of applications. However, it is important to note that the natural rubber (NR) compound formulation used in this work represents only a basic composition and can be further tailored to achieve enhanced mechanical properties, if required.

3.3. Morphology of PALF Leather

SEM micrographs of UPALF and TPALF leather with varying ENR content are presented in Figure 8. In the absence of ENR in the PALF leather samples, UPALF leather displayed a clear separation between the rubber and fiber layers, with visible fibers escaping from the sample. In contrast, TPALF leather exhibited slightly better compatibility between the rubber and fiber layers. This improved compatibility can be attributed to the inherent incompatibility between the hydrophobic nature of rubber and the hydrophilic nature of the fibers, a phenomenon observed in other polymer composite research [20].

However, when the fibers were treated with a NaOH solution, better latex absorption and dispersion in the fiber sheet occurred. As a result, the TPALF leather exhibited more rubber-like properties, including enhanced flexibility, elongation, and tear resistance, as observed in the mechanical properties results presented earlier.

With the addition of ENR, the compatibility between the rubber and fibers significantly improved. The previous separation between rubber and fibers observed in the samples without ENR disappeared. Instead, an even and uniform distribution of fibers

within the rubber matrix became evident, especially with only 5% ENR applied. In this context, UPALF and TPALF leather samples with ENR showed minimal differences. These results underscore the positive impact of ENR on enhancing the compatibility between rubber and fibers, which, as previously shown, directly contributes to the improvement of mechanical properties.

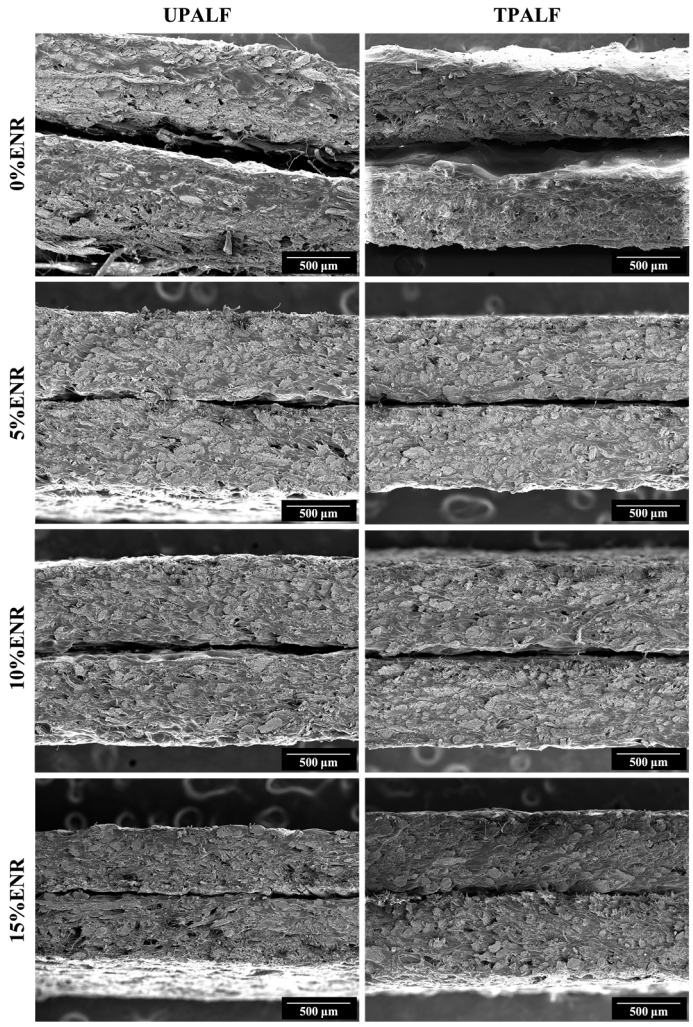

Figure 8. SEM micrograph of the cross-sectional morphology of PALF leather from non-woven fibers sheets containing different amounts of ENR.

3.4. Colors of the PALF Leather

Figure 9a illustrates the lightness (L*) and color appearance of PALF leather samples, while Figure 9b presents the color coordinates of the samples, reported as values a* and b*. Positive a* values indicate redness, and positive b* values indicate yellowness. Conversely, negative values represent greenness (a*) and blueness (b*). A summary of all the results is provided in Table 3.

The lightness values of the PALF leather without ENR tended to increase from 73.48 to 75.23, or a 2.4% increase, when the PALF fibers were treated with a NaOH solution. Alkaline-treated PALF fibers effectively removed impurities and binders, such as hemicellulose and lignin, from the surface. This process resulted in whiter and brighter fibers, contributing to the enhanced brightness of the TPALF leather.

All the PALF leather samples displayed color values falling within the yellow and red range, reflecting the base colors of the rubber and PALF fibers. Notably, the color of the TPALF leather with alkaline-treated fibers tended to exhibit a more pronounced yellow hue compared with the UPALF leather. This difference can be attributed to the inherent

off-white color of the TPALF fibers, which did not significantly alter the rubber color, unlike the UPALF fibers, which are darker in color.

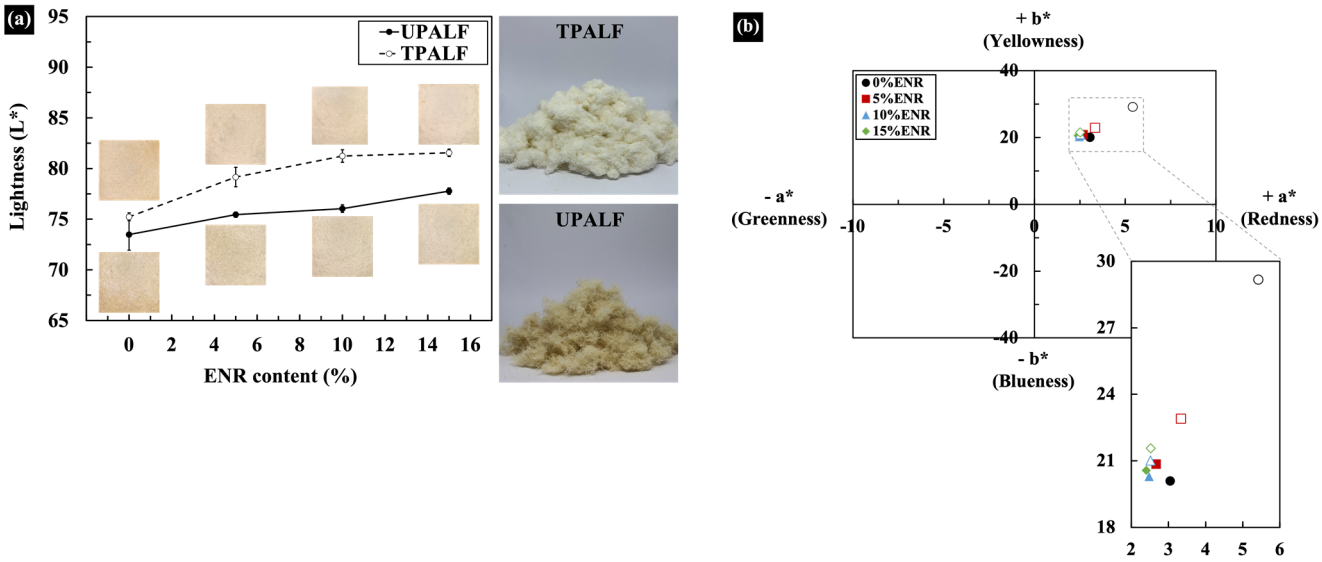

Figure 9. Lightness (**a**) and color values (**b**) of UPALF leather (closed symbols) and TPALF leather (open symbols) containing different amounts of ENR, where L*, a*, and b* indicate the lightness, redness, and yellowness values, respectively.

Table 3. Color value from CIELAB measurements of the PALF leathers containing different amounts of ENR.

Sample	ENR Content (wt.%)	L*	a*	b*
UPALF	0	73.48	3.04	20.10
	5	75.45	2.66	20.86
	10	76.04	2.48	20.29
	15	77.77	2.40	20.57
TPALF	0	75.23	5.42	29.17
	5	79.16	3.33	22.89
	10	81.24	2.52	21.01
	15	81.55	2.52	21.57

Additionally, both PALF leather variants demonstrated an increase in lightness values and a decrease in yellowness as the ENR content increased. This phenomenon likely resulted from improved compatibility between the rubber and fibers, leading to a greater manifestation of the fiber color in the artificial leather. The achieved lightness values in PALF leather can be advantageous for finishing or coloring the leather without distorting the color, expanding the range of potential applications.

3.5. Comparison of PALF Leather Properties with Commercial Alternatives

The current trend in the leather industry emphasizes the use of natural materials as alternatives to animal skins for leather production. In this context, our goal is to present an efficient production process and highlight the properties of self-produced PALF leather derived from non-woven pineapple leaf fiber sheets. To achieve this, we conducted a comprehensive comparison of tensile strength, tear resistance, and hardness with various commercial leathers based on the literature data [3].

As shown in Table 4, our research findings indicate that the PALF leather in this study exhibits significantly higher tensile strength and tear resistance when compared with other leather materials. These alternatives include Muskin (derived from *Phellinus ellipsoideus mushrooms*), Pinatex (sourced from pineapple leaf fibers), and various commercial leathers

such as Kombucha (made from a symbiotic culture of bacteria and yeast), Vegea (produced from grape waste material), and Teak Leaf (derived from teak leaves). While PALF leather may have only slightly lower tensile strength when compared with materials like Appleskin (from apple waste) and Desserto (made from milled cactus leaves), it still demonstrates superior tear resistance.

Table 4. Mechanical properties of PALF leather compared with other leather alternatives.

Sample	Tensile Strength (MPa)	Tear Strength (N/mm)	Hardness (Shore A)	Ref.
PALF leather	12.3	56.7	75.8	This work
Real leather	39.5	82.9	not reported	[3]
Real leather *	17.2	55.9	57.3	*
Pinatex	4.5	31.0	not reported	[3]
Pinatex *	not measured	30.4	40.9	*
Muskin	0.2	0.5	not reported	[3]
Desserto	20.8	37.2	not reported	[3]
Appleskin	14	18.4	not reported	[3]
PU leather *	10.6	34.4	45.7	*

* self-measurements.

Comparing PALF leather to genuine leather, we observe that PALF leather has slightly lower tensile strength and tear resistance. However, according to our self-measurements in this study, PALF leather's tensile and tear strength are not significantly different from those of genuine leather and remain higher than Pinatex and PU leather. In terms of hardness properties, PALF leather, produced from non-woven pineapple fibers, exhibits a relatively high fiber density with fewer gaps or bubbles than other commercial leathers like Desserto and Pinatex. Consequently, this results in slightly higher hardness compared with genuine leather and other commercial alternatives. However, there is room for improvement in terms of softness, which could potentially be achieved by adjusting the leather's internal structure and the formulation of the NR compounds.

Remarkably, the literature highlights the presence of harmful substances in many commercial leathers [3,47]. In contrast, our work employs a straightforward preparation process, utilizing basic chemicals typically found in standard rubber products. The ENRs used to improve compatibility in this work are also prepared in an environmentally friendly manner [27]. Taking all these factors into account, it can be concluded that PALF leather represents a sustainable leather alternative with the potential to effectively replace genuine leather and other commercial leather products.

3.6. Application Example of PALF Leather

In today's world, manufacturers of leather products such as shoes and bags are increasingly opting for vegan or artificial leather made from natural materials to replace animal skins. This shift not only avoids harm to animals but also contributes to a more environmentally friendly and sustainable material choice.

As discussed earlier, the PALF leather produced in this research exhibits relatively high mechanical properties, making it a suitable alternative to the synthetic leather available in the market. What makes it even more appealing is that the chosen materials are natural and originate from agricultural waste, making the process more environmentally friendly and sustainable. Moreover, the production process is straightforward.

In this study, we provide an example of how PALF leather can be used in practical applications. Figure 10 illustrates an experiment where PALF leather was used to create shoes, serving as a model for its potential applications. Additionally, we explored customizing colors to offer a wider range of options for users. These experiments involved using natural materials like carrot pulp, spent Thai red tea powder, and spent coffee grounds to achieve intriguing color tones. Furthermore, we demonstrated a simple method for creating patterns on the leather surface, achieving a realistic leather appearance.

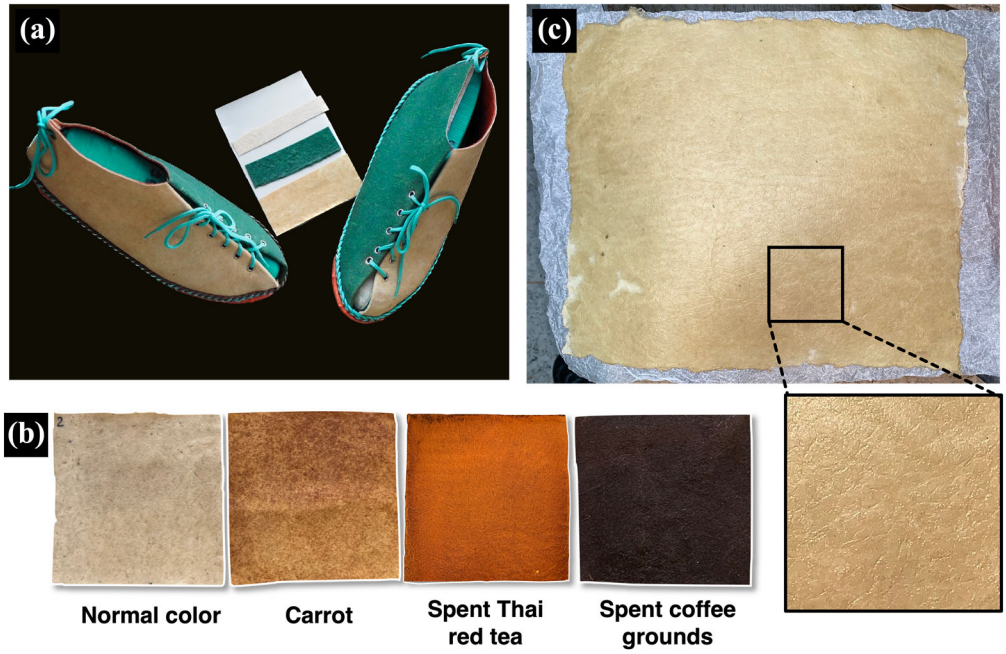

Figure 10. Prototype footwear made from PALF leather (**a**), customizing the color of PALF leather using different wastes (**b**), and A3 size (297 mm × 420 mm) PALF leather with embossed pattern (**c**). Picture (**a**) courtesy of Ornwipa Mongkondaw.

PALF leather can be produced in a laboratory setting, yielding sheets of up to approximately A3 size (297 mm × 420 mm), offering ample material for a variety of applications, albeit within the constraints of oven size limitations. Given the straightforward nature of this technology, it holds the potential to be readily transferred to local communities, enabling them to craft a diverse range of products.

4. Conclusions

In this study, we have successfully demonstrated the production of PALF leather by blending natural rubber and pineapple leaf fibers, yielding a versatile artificial leather with customizable properties. A 50/50 NR/PALF ratio provides a balanced combination of strength and tactile comfort suitable for various applications. Alkaline-treated fibers enhance flexibility, elongation, and tear resistance in TPALF leather, while UPALF leather offers increased tensile strength and modulus. The incorporation of a small amount of epoxidized natural rubber (ENR) significantly improves the mechanical properties. Moreover, our work addresses the common issue of component separation in commercial artificial leather, opening up new possibilities for its application. This research showcases a sustainable and economically viable alternative to traditional leather, with the potential to revolutionize the leather industry and contribute to a more environmentally friendly future.

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Conflicts of Interest: T.A. declares a conflict of interest related to this research article. As a university professor at Mahidol University, I have been engaged in developing an innovative method for extracting pineapple leaf fiber. This endeavor led to the establishment of TEAnity Team Co. Ltd., where I hold the position of chief technology officer (CTO). While this research was conducted independently and supported solely by government and university funding, I acknowledge the potential for a conflict due to my dual roles. I affirm that the research and findings presented in the article remain unbiased and have not been influenced by any financial interests or affiliations with TEAnity Team Co., Ltd.

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