

Impregnation of Poly(lactic acid) on Biologically Pulped Pineapple Leaf Fiber for Packaging Materials

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Newly developed packaging paper made of biopulped pineapple leaf fiber (PALF) and poly(lactic acid)(PLA) was studied. PALF packaging sheets were solvent impregnated with PLA at different concentrations in order to improve their moisture barrier and mechanical performance. With the impregnation of PLA at a concentration of 4%, the packaging material exhibited a low moisture uptake and a high tear index. An electron micrograph of the sample at 4% impregnation revealed uniform and packed PLA reversed microsphere morphology. These results suggest that surface coating *via* biodegradable polymers, such as PLA, may be utilized for manufacturing packaging materials in industrial applications. This new packaging material could reduce the dependency on wood-based paper and plastic-based packaging.

Keywords: Pineapple leaf fiber; Poly(lactic acid); Coating; Impregnation; Paper; Packaging materials

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INTRODUCTION

Explorations of the potential use of agro-waste crops and lignocellulosic materials as the alternative source of fiber materials for pulp and paper applications have been reported throughout the literature. This is driven by the depletion of wood resources worldwide and the growing environmental awareness. Pineapple leaf fiber (PALF) is one of the potential alternative fiber resources, as it is abundantly available especially in tropical countries, such as Malaysia (Ashori 2006). Table 1 presents the chemical composition of Malaysian PALF (Nadirah *et al.* 2012).

Table 1. Chemical composition of PALF

Chemical composition	%
Ash	4.73
Cellulose	74.33
Holocellulose	80.68
Lignin	10.41
Extractives	6.68

The leaves of the pineapple plant yield fibers that are strong, white, fine, and silky (Chollakup *et al.* 2011), and display excellent paper making properties (Nayan *et al.* 2013). PALF exhibits superior fiber strength due to its high cellulose content (70 to 82%) and well-separated filaments (Buana *et al.* 2013).

Mercerization, sometimes referred to as alkali treatment, is the process of subjecting a cellulose fiber to interact with a relatively concentrated aqueous solution of a strong base (Tarbuk *et al.* 2014). Though this chemical pulping method is widely used, there are concerns regarding its cost and environmental impact.

Another approach to pulping that has gained much interest is biological pulping, or biopulping. In biopulping, lignocellulosic materials are treated with natural wood decay fungi prior to thermomechanical pulping. In the biopulping process, the lignocellulosic material, which is composed of lignin, hemicelluloses, and cellulose, is subjected to enzymatic (fungi) attack especially white-rot fungi. Such treatment is effective in degrading the holocellulose structure and depolymerized the lignin (Singhal *et al.* 2015). Lignin creates a protective sheath around cellulose. Therefore, the removal of lignin, or delignification, is an essential for the conversion of lignocellulosic materials, such as PALF, into pulp. Recently, the effectiveness of biopulping PALF with the use of *Ceriporiopsis subvermispota* has been shown (Nayan *et al.* 2014). Although good paper-packaging properties were achieved, inherent cellulosic disadvantage was still an issue for viable use.

The strength of paper and cellulose-based packaging are strongly influenced by their absorption of moisture. High moisture absorption occurs due to the hydrogen bonding of water molecules to the hydroxyl groups within the fibers' cell wall, thus reducing the physical and mechanical strength of the paper and paperboard, which causes loss of mechanical integrity during storage and distribution (Papadopoulou *et al.* 2014; Wang *et al.* 2014; Yahya and Yusof 2014). Therefore, it is encouraging to further enhance the PALF sheets with a biopolymer that possesses good mechanical strength and hydrophobicity.

One of the most promising biopolymers for such a purpose is poly(lactic acid) (PLA) because it has good performance characteristics as a packaging material, along with being biodegradable, biocompatible, and commercially available (Butkinaree *et al.* 2008; Zhang *et al.* 2014). PLA is becoming an important alternative as a green packaging material because it performs better than synthetic plastics in many applications (Pikoń and Czop 2014).

Paperboards coated with PLA revealed good water resistance and comparable strength to that of polyethylene-coated paperboards (Rhim and Kim 2009). Many reports focus on the fabrication of biocomposite, in which PLA functions as the matrix and PALF as the fibrous reinforcement (Kaewpirom and Worrarat 2014; Shih *et al.* 2014; Neto *et al.* 2015).

Thus far, there have been no reported studies on paper packaging sheets made of pineapple leaf fiber/poly(lactic acid) (PALF/PLA). We expected that the properties of PALF sheets could be enhanced by the surface impregnation with PLA. Therefore, our main goal was to impede the moisture activity of PALF while enhancing its mechanical properties. Initially, the PALF was pulped using white rot fungi, *Ceriporiopsis subvermispota*. Then it was formed into sheets and the sheets were impregnated with PLA at various concentrations.

EXPERIMENTAL

Biopulping of PALF

Waste PALF (leaf of *Ananas comosus*, Josapine hybrid) was individually separated and cleaned by hand and then chopped into a uniform size (of approximately 10 cm). Cultures of *Ceriporiopsis subvermispora* were grown at 28 °C for 10 days in 300 mL flasks containing 50 mL of medium, which contained 1% birchwood xylan supplemented with 0.2% yeast-extract. Each flask was autoclaved for 15 min at 120 °C. After cooling, each flask was inoculated with 0.1% inoculum on a dry-weight basis. The culture fluid containing extracellular proteins was centrifuged for 20 min at 6000 rpm to remove the mycelium and the extracellular glucan. The supernatant was filtered through filter paper, and then was freeze-dried and subsequently dissolved in distilled water. The chopped PALF were immersed in the media containing 0.25% of fungus (dry-basis). The biodegradation process occurred for 3 weeks at a temperature of 28 °C. Afterwards, the PALF was washed with running tap water. The delignification process is depicted in Fig. 1. The PALF pulp was formed into paper sheets by hand and the sheets were kept at 23 °C and 50% RH for at least 24 h before testing.

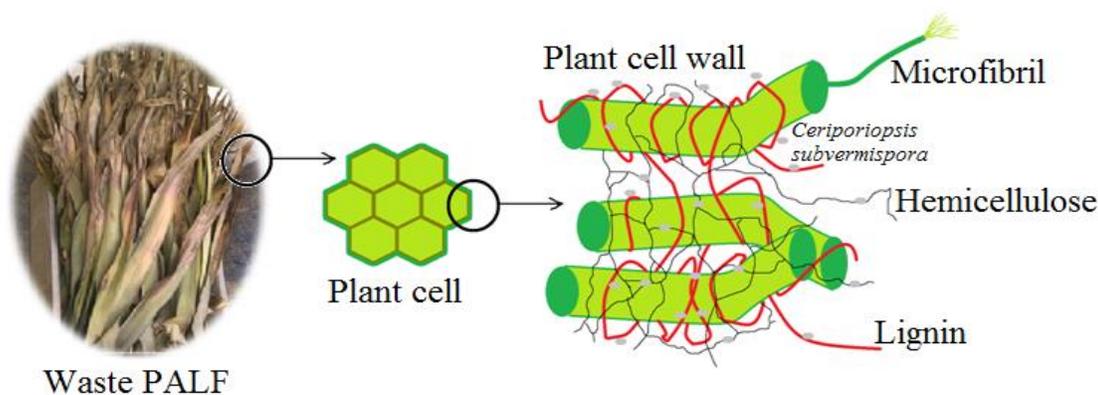


Fig. 1. Delignification mechanism of PALF via *Ceriporiopsis subvermispora* fungus

Impregnation of PLA on PALF

The PLA (Nature Works™ 4031 D) was supplied by Nature Works LLC, USA. Its molecular weight (M_w) was between 195000 and 205000 g/mol. The PLA granules were mixed into methylene chloride (Merck) at various concentrations (1%, 2%, 4%, and 6% w/v), and the polymeric solutions were mechanically stirred overnight at 50 rpm. The initially prepared PALF were immersed into the solutions containing PLA for 5 min. The impregnated PALF were then placed in a fume hood under ambient conditions to allow evaporation of the organic solvent.

Characterizations

The tear test was performed using the Elmendorf Tear method (ASTM D-1922). The tear index was calculated using Eq. 1,

$$\text{Tear index} = \text{average tearing force (N)} / \text{average grammage (kg/m}^2\text{)} \quad (1)$$

whereby the average tearing force was calculated using Eq. 2.

$$\text{Average tearing force} = 16 \times 9.81 \times \text{average scale reading} \quad (2)$$

The bursting test was performed on a Mullen type tester according to ASTM D774. The burst index was calculated using Eq. 3.

$$\text{Burst index} = \text{bursting strength (kPa)} / \text{average grammage (g/m}^2\text{)} \quad (3)$$

At least five replicates were done for each sheet type in both mechanical tests. The sheet morphology was examined using a scanning electron microscope (SEM) (Leo Supra 50VP Field Emission SEM, Carl Zeiss, Germany). The moisture absorption test was done on triplicate sheet samples of 2×2 cm, in which the samples were placed on top of a wire mesh in an environment with a relative humidity (RH) of 53% conditioned in desiccators in accordance to ASTM E-104 standards. The RH environment was controlled using a saturated salt solution of magnesium nitrate. The samples were weighed at intervals of six hours until they were saturated. The percentage of moisture absorption was calculated using Eq. 4,

$$M_t (\%) = (W_w - W_d) / W_d \times 100 \quad (4)$$

where M_t is the moisture absorption (%) of the sample, and W_w and W_d are the weights of the sample before and after its exposure in the controlled RH, respectively.

The water-wetting test was performed on square PALF/PLA samples. A drop of water was allowed to fall from a burette with an approximate height of 1.0 cm from the sample. The time required to wet a 1 cm distance was recorded with a stopwatch. At least three replications were done for each PALF/PLA type.

Fourier transform infrared (FTIR) spectra of the samples were obtained using a Perkin Elmer Spectrum System 2000 FTIR (USA).

RESULTS AND DISCUSSION

Tear and Burst Indices

Mechanical properties of the prepared PALF sheets, which were impregnated with different concentrations of PLA, are shown in Table 1. The tear index is a measure of the ability of the sheet to withstand a tearing force (Nayan *et al.* 2013). The control biologically pulped PALF sheet exhibited a tear index value of about $2.4 \text{ Nm}^2/\text{kg}$. This was attributed to the biopulping process of the PALF, which rendered a better crystalline structure compared to the conventionally mercerized PALF ($1.9 \text{ Nm}^2/\text{kg}$) (Nayan *et al.* 2013). Impregnation of the PALF with 1% PLA solution (PALF/1PLA) showed no significant changes to its tear index. The minimal amount of PLA caused the surface to be dominated by solvent, thereby leaving behind a substantial portion of bare PALF. This discontinuous PLA formation rendered no improvement towards the sheet tear index. However, increasing the concentration of PLA in the solution to 2% (PALF/2PLA) led to a notable improvement in the tear index. The highest tear index was achieved at $3.5 \text{ Nm}^2/\text{kg}$ by the sample impregnated with 4% PLA solution (PALF/4PLA). At these PLA concentrations, the biodegradable polymer formed a continuous layer on the PALF surface that reinforced the sheet by impeding the tear propagation. Upon a higher impregnation concentration of 6% (PALF/6PLA), the increase in the tear index stopped. This was due to the weak spots

during the mechanical testing caused by the excessive PLA coating, as well as by the weight of the PLA. The weight of the PLA contributed to the lowering of tear index due to the specific weight relation of the testing.

The burst index represents how much pressure a paper sheet can tolerate before it ruptures. In Table 2, it can be seen that the PLA became effective at 2% concentration. The burst index of the PALF samples improved significantly with impregnation of 2% PLA solution and became stable with higher concentrations. The PLA acted as load bearing component, and sufficiently resisted perpendicular pressure. In this case, the expected adverse relation of burst index (reduction) was not observed but the increase was slight compared to tear index. This means that the interaction is adequate enough to hinder any loss in burst index. Both tests proved that with an optimum concentration of PLA solution, impregnated PALF sheets with good mechanical properties could be achieved.

Table 2. Tear and Burst Indices of PALF and PALF/PLA

Sample	Tear index (Nm ² /kg)	Burst index (kPa·m ² /g)
PALF	2.4 ± 0.3	2.4 ± 0.3
PALF/1PLA	2.3 ± 0.4	2.6 ± 0.9
PALF/2PLA	3.1 ± 0.6	3.2 ± 0.8
PALF/4PLA	3.5 ± 0.2	3.2 ± 0.4
PALF/6PLA	2.8 ± 0.8	3.3 ± 0.8

Morphological Analysis

Figure 2a depicts the SEM image of the control PALF paper sheet. The sample exhibited typical surface features of lignocellulosic fibers. Thickness values of the PLA layers on the PALF were measured to be 20.2, 26.5, 59.8, and 77.9 microns for 1, 2, 4, and 6% PLA coating, respectively. A uniform PLA surface coating can be seen in the PALF/4PLA sample, which is shown in Fig. 2b. The entire surface of the PALF/4PLA sample had been covered with PLA by solution dipping, and no exposed PALF surface was observed. This is a positive indication of a possible way to obtain strong packaging sheets while preserving their fiber characteristics. PLA, a biopolymer that is easy to process and has high mechanical strength, provided the reinforcement needed by the PALF. Higher magnification on the surface of the PALF/4PLA sample (Fig. 2c) revealed uniform internal dimple-like patterns, as a result of solvent evaporation (Kim *et al.* 2010). These micron sized pores enhanced the hydrophobicity of the PALF surface. Furthermore, these dimples were closely packed with average internal diameters of 1.7 μm.

Moisture Absorption

Figure 3 presents the moisture uptake of the unimpregnated and impregnated PALF sheets. It can be seen that the PLA modified PALF showed a substantial reduction of moisture uptake in the PALF/2PLA samples. The hydrophobic features of the PLA components that surround the PALF surfaces explain this reduction. Furthermore, the closely packed PLA micro dimples, which can be seen in Fig. 2c, enabled the PLA to act as barriers, thus preventing contact between the water molecules and the PALF surface hydroxyl groups. Utilization of a biopolymer coating on the PALF reduced the degree of water uptake, which in turn could preserve the functional, structural, and mechanical properties of the sheets.

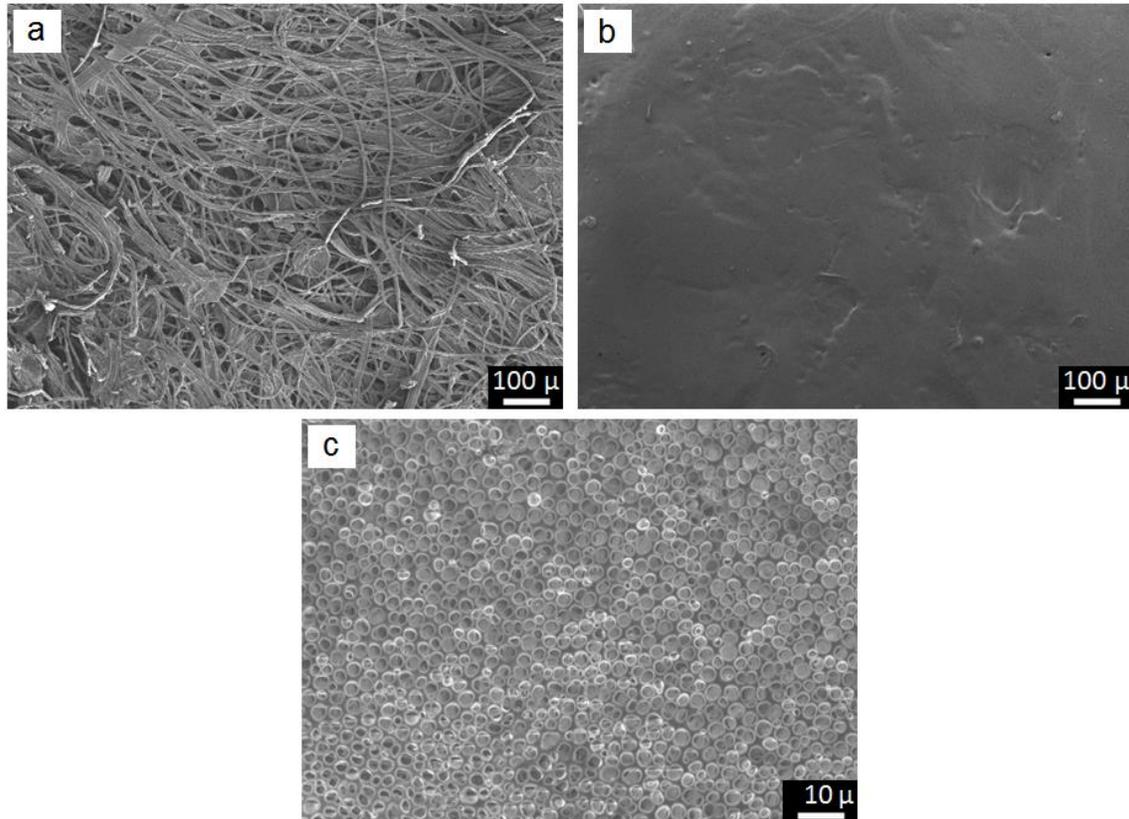


Fig. 2. SEM images of a) control PALF, b) PALF/4PLA, and c) higher magnification of PALF/4PLA

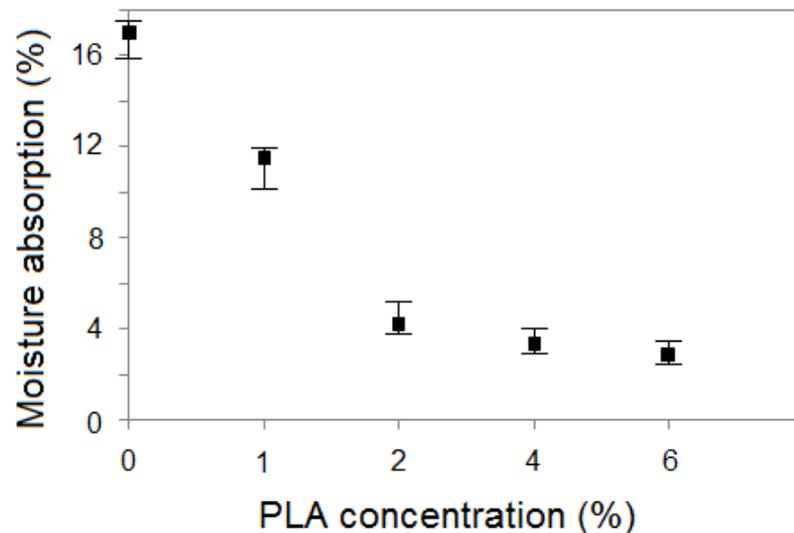


Fig. 3. Moisture absorption of PALF/PLA with varying PLA concentrations

Water Wetting Time

The wetting times of the control PALF and PALF/PLA are presented in Table 3. Figure 4 depicts the water-wetting test of the samples after 1s. The water droplet wetted the control PALF instantaneously. The PALF/1PLA sample delayed the wetting time up to 20 to 30 s. The PALF paper sheets impregnated with 2, 4, and 6% PLA solutions showed no water migration up to more than 24 h. This indicated that the PLA coating induced an

effective water barrier for the PALF surface. This corresponds to the presence of hydrophobic PLA, which decreased the surface tension of the PALF by providing it a high mismatch of surface tension between the water, thus making it more difficult for the water molecules to wet the PALF surface. This suggests that the PLA was suitable for increasing the water resistance of the PALF.

Table 3. Wetting Time of PALF/PLA

Sample	Wetting time
PALF	1 s
PALF/1PLA	20-30 s
PALF/2PLA	>24 hr
PALF/4PLA	>24 hr
PALF/6PLA	>24 hr

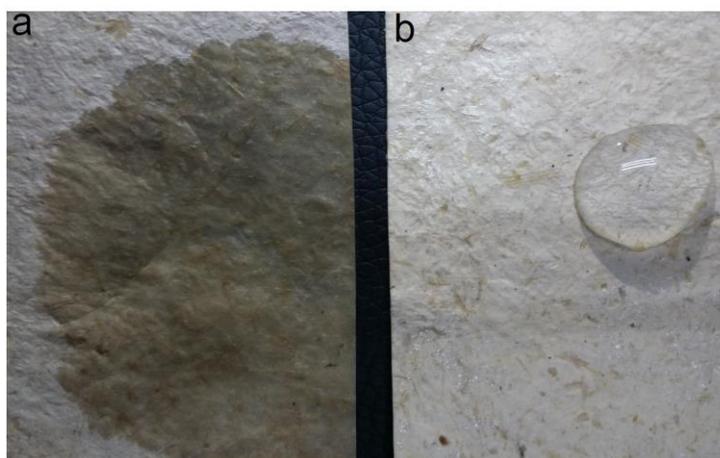


Fig. 4. Water wetting test of a) control PALF and b) PALF/4PLA after 1 s

FTIR Spectroscopy

The FTIR spectrum of the control PALF in Fig. 5a exhibits a band at 3400 cm^{-1} , which represents the intermolecular and intramolecular H bonds of free OH in cellulose. Figure 5a also displays a C-H stretching peak at 2900 cm^{-1} , as well as a peak at 1700 cm^{-1} , which represents the C=O stretching (acetyl group of hemicellulose and ester linkage of lignin). These IR vibrations are in agreement with the functional groups of lignocellulosic fiber (Razak *et al.* 2014). It can be seen that the impregnation of 4% PLA (Fig. 5b) resulted in lower detection of the OH band compared with that of the control PALF. This is due to the PLA coating since it further limited the exposed cellulose surfaces. The 1700 cm^{-1} peak (representing the acetyl groups of PLA) seemed to be increased with the treatment, indicating that the PALF surfaces had been dominated by the hydrophobic functional group of the PLA, thus reducing the environmental moisture uptake. Noticeably a new peak emerged at 1450 cm^{-1} , which represented the CH_3 band. This was due to the considerable amount of PLA present on the PALF. The proposed PALF-PLA interactions are illustrated in the insert of Fig. 5.

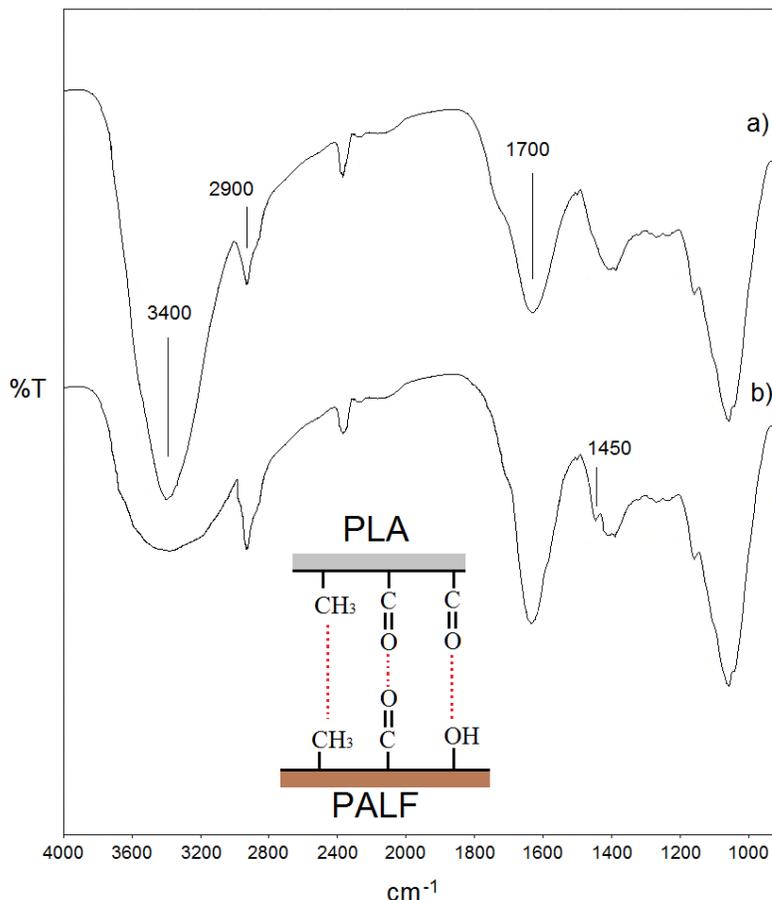


Fig. 5. FTIR spectra of a) control PALF b) PALF/4PLA

CONCLUSIONS

1. Biopulped PALF has the potential to be used as a paper packaging material when it is impregnated with PLA. The optimum PLA concentration (4%) proved to be suitable for the preparation of PALF/PLA sheets. This was established by the samples' low moisture uptake, good wetting time, high mechanical properties, uniform sheet formation on a microscopic level, and good PALF-PLA interaction.
2. The ease of forming these sheets, as well as their economic value, presented a high potential for these sheets being produced on a large-scale. Promise is shown in packaging applications that require the utilization of bio-derived resources and must be economically cost-effective. The main advantage of this newly developed PALF/PLA paper is that the fiber source can be obtained from the by-product of harvesting the pineapple fruit.

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REFERENCES CITED

- Ashori, A. (2006). "Non-wood fibers-A potential source of raw material in paper making," *Polymer-Plastics Technology and Engineering* 45(10), 1133-116. DOI: 10.1080/03602550600728976
- ASTM D1922-09. (2009). "Standard test method for propagation tear resistance of plastic film and thin sheeting by pendulum method," ASTM International, West Conshohocken, PA. DOI: 10.1520/D1922-09
- ASTM D774/ D774M. (2002). "Standard test method for bursting strength of paper," ASTM International, West Conshohocken, PA. DOI: 10.1520/D0774_D0774M-97R02
- ASTM E104-02. (2012). "Standard practice for maintaining constant relative humidity by means of aqueous solutions," ASTM International, West Conshohocken, PA. DOI: 10.1520/E0104-02R12
- Buana, M. S. A. S., Pasbaskhsh, P., Goh, K. L., Bateni, F., and Haris, M. R. H. M. (2013). "Elasticity, microstructure and thermal stability of foliage and fruit fibres from four tropical crops," *Fibers and Polymers* 14(4), 623-629. DOI: 10.1007/s12221-013-0623-4
- Butkinaree, S., Jinkarn, T., and Yoksan, R. (2008). "Effect of biodegradable coating on barrier properties of paperboard food packaging," *Journal of Metals, Materials and Minerals* 18(219-222).
- Chollakup, R., Tantatherdtam, R., Ujjin, S., and Sriroth, K. (2011). "Pineapple leaf fiber reinforced thermoplastic composites: Effects of fiber length and fiber content on their characteristics," *Journal of Applied Polymer Science* 119(4), 1952-1960. DOI: 10.1002/app.32910
- Kaewpirom, S., and Worrarat, C. (2014). "Preparation and properties of pineapple leaf fiber reinforced poly (lactic acid) green composites," *Fibers and Polymers* 15(7), 1469-1477. DOI: 10.1007/s12221-014-1469-0
- Kim, M. R., Lee, S., Park, J. K., and Cho, K. Y. (2010). "Golf ball-shaped PLGA microparticles with internal pores fabricated by simple O/W emulsion," *Chemical Communications* 46(39), 7433-7435. DOI: 10.1039/c0cc01738h
- Nadirah, W. O. W., Jawaid, M., Al Masri, A. A., Kalil, H. P. S. A., Suhaily, S. S. and Mohamed, A. R. (2012). "Cell wall morphology, chemical and thermal analysis of cultivated pineapple leaf fibres for industrial application," *Journal of Polymers and the Environment* 20(2), 404-411. DOI:10.1007/s10924-011-0380-7
- Nayan, N. H. M., Razak, S. I. A., Rahman, W. A. W. A., and Majid, R. A. (2013). "Effects of mercerization on the properties of paper produced from Malaysian pineapple leaf fiber," *International Journal of Engineering and Technology* 13(4), 1-6.
- Nayan, N. H. M., Razak, S. I. A., and Rahman, W. A. W. A. (2014). "Biopulping by *Ceriporiopsis subvermispora* towards pineapple leaf fiber (PALF) paper properties," *Advanced Materials Research*. 1043, 180-183. DOI:10.4028/www.scientific.net/AMR.1043.180
- Neto, A. R. S., Araujo, M. A. M., Barboza, R. M. P., Fonseca, A. S., Tonoli, G. H. D., Souza, F. V. D., Mattoso, L. H. C., and Marconcini, J. M. (2015). "Comparative study of 12 pineapple leaf fiber varieties for use as mechanical reinforcement in polymer composites," *Industrial Crops and Products* 64, 68-78. DOI: 10.1016/j.indcrop.2014.10.042

- Papadopoulou, E., Bikiaris, D., Chrysafis, K., Wladyka-Przybylak, M., Wesolek, D., Mankowski, J., Kolodzie, J., Baraniecki, P., Bujnowicz, K., and Gronberg, V. (2014). "Value-added industrial products from bast fiber crops," *Industrial Crops and Products* 68, 116-125. DOI: 10.1016/j.indcrop.2014.10.028
- Pikoń, K., and Czop, M. (2014). "Environmental impact of biodegradable packaging waste utilization," *Polish Journal of Environmental Studies* 23(3), 969-973.
- Razak, S. I. A., Sharif, N. F. A., and Muhamad, I. I. (2014). "Polyaniline coated halloysite nanotubes: Effect of para-hydroxybenzene sulfonic acid doping," *Composite Interfaces* 21(8), 715-722. DOI: 10.1080/15685543.2014.932551
- Rhim, J. W., and Kim, J. H. (2009). "Properties of poly(lactide)-coated paperboard for the use of 1-way paper cup," *Journal of Food Science* 74(2), 105-111. DOI: 10.1111/j.1750-3841.2009.01073.x
- Shih, Y. F., Huang, R. H., and Yu, Y. H. (2014). "Preparation and characterization of sol-gel-modified pineapple leaf fiber/poly(lactic acid) composites," *Journal of Sol-Gel Science and Technology* 70(3), 491-499. DOI: 10.1007/s10971-014-3311-y
- Singhal, A., Jaiswal, P. K., and Thakur, I. S. (2015). "Biopulping of bagasse by *Cryptococcus albidus* under partially sterilized conditions," *International Biodeterioration & Biodegradation* 97, 143-150. DOI: 10.1016/j.ibiod.2014.10.011
- Tarbuk, A., Grancaric, A. M., and Leskovac, M. (2014). "Novel cotton cellulose by cationization during mercerization-Part 2: The interface phenomena," *Cellulose* 21(3), 2089-2099. DOI: 10.1007/s10570-014-0245-z
- Wang, Y. Y., Tian, M., Xu, H. X., and Fan, P. (2014). "Influence of moisture on mechanical properties of cellulose insulation paper," *International Journal of Modern Physics B* 28(7), 1450051. DOI: 10.1142/S0217979214500519
- Yahya, S. A., and Yusof, Y. (2014). "Utilization of pineapple leaf fiber as technical fibers," *Applied Mechanics and Materials* 470, 112-115. DOI: 10.4028/www.scientific.net/AMM.470.112
- Zhang, W., Hua, D., Ma, S., Chen, Z., Wang, Y., Zhang, F., Len, F., and Pu, X. (2014). "Preliminary study for vascular tissue engineering by Electrospinning angelica polysaccharide (ASP)/PLA microfibrinous scaffolds," *International Journal of Polymeric Materials* 63(13), 672-679. DOI: 10.1080/00914037.2013.854241

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