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Moisture Absorption and Thermal Properties of Unidirectional Pineapple Leaf Fibre/Polylactic Acid Composites under Hygrothermal Ageing Conditions

Zaleha Mustafa[1,*], Anira Shahidah Razali[1], Thavinnesh Kumar Rajendran[1], Siti Hajar Sheikh Md Fadzullah[2], Sivakumar Dhar Malingam[2], Toibah Abd Rahim[1], Thanate Ratanawilai[3]

[1] Fakulti Kejuruteraan Pembuatan, Universiti Teknikal Malaysia Melaka, Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, Malaysia
[2] Fakulti Kejuruteraan Mekanikal, Universiti Teknikal Malaysia Melaka, Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, Malaysia
[3] Department of Industrial and Manufacturing Engineering, Faculty of Engineering, Prince of Songkla University, Hat Yai, 90112 Songkhla, Thailand

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ABSTRACT

In this study, the effect of fibre content on moisture absorption and thermal properties of pineapple leaf fibre (PALF) reinforced polylactic acid (PLA) at elevated temperature and humidity was assessed. The unidirectional PALF/PLA composites were fabricated by using pre-pregging technique and compressed moulded to produce composites with two fibre loadings (40 and 60 wt. %). The composite was saturated in a humidity chamber that contains 90% relative humidity at 50°C for 30 days. The effect of different fibre loading on moisture absorption was measured through moisture uptake. Their thermal stability and thermal characteristic were evaluated by using thermal gravimetric analysis (TGA) and differential scanning analysis (DSC). The result showed that moisture absorption increases with the increase of fibre content and follows Fickian Law. The presence of PALF reduces the initial thermal degradation of the neat PLA as well as promoted the crystallization of the PLA. Upon exposure to the high temperature and humidity, the value glass transition temperature (Tg) and melting temperature (Tm) of the neat PLA and PALF/PLA composites shifted to the lower temperature possibly due to hydrolytic degradation in the composite structure.

1. Introduction

Interest in using biopolymers and natural fibre in composite materials as possible replacements for traditional fuel-based polymers has been growing in the past decade due to an increase in the environmental concern and sustainability of the materials. Polylactic acid (PLA) has been widely used due to its excellent physical and mechanical qualities, biodegradability, and accessibility [1-4]. The natural fibre is often utilised as reinforcement owing to its flexibility, high specific strength, low cost and as well as to maintaining the biodegradability properties of the composite [5-7].

* *Corresponding author.*
E-mail address: zaleha@utem.edu.my

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Among the well-known natural fibre plants, pineapple leaf fibre (PALF) is by far one of the most promising reinforcements in biocomposites. PALF has a desirable characteristic to be used for reinforcement as it contains a low percentage of lignin contents (5–12 wt. %) as well as high cellulose content (70–82 wt. %) and low micro-fibril angle [6,8,9]. Thus, producing outstanding tensile strength (172-1627 MPa) while the modulus can reach up to 8.2 GPa [2,7]. However, their usage and studies in polymer matrix composite are still limited and have not yet garnered much attention as compared to more popular natural fibres such as jute, kenaf and others [10].

The application of the degradable polymer and composite depends on their durability during application. The degradation mechanism is the key factor to determine their lifetime. It will be comparable to 10 years in life service should that polymeric materials can retain their mechanical performance for at least 60 weeks in an environment containing high humidity (90%) and temperature (50°C) [11,12]. The biodegradable PLA even though is hydrophobic, they are humidity sensitive at a higher temperature and may induce a higher hydrolysis rate. Natural fibre, being hydrophilic is susceptible to water absorption and may swell causing dimensional changes to the composite upon exposure to water or moisture.

To our knowledge, there has not been much research on thermal stability and the influence of fibre loading on the thermal properties of PLA and PALF/PLA composites at high temperatures and humidity in the literature. Thus, in this study, moisture absorption behaviour and thermal properties of the PALF/PLA composites were investigated by observation of the weight intake, thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) to evaluate the degradative manners of the composite and effect of fibre contents on their thermal characteristic.

2. Methodology

2.1 Materials

The PALF fibre is used in the form of 2 plies yarn with a density of 1.526 g/cm³ (Figure 1a). The fibres were alkaline treated with 5 wt. % NaOH as previously reported [13]. The PLA grade 6100D is used as the matrix (Nature works, USA). The chemicals were purchased from Sigma Alrich (USA) with a 99.95 purity grade.

2.2 Sample Preparation

The PLA granule was dissolved in chloroform solution at a ratio of 1:2 and the mixtures were stirred for at least 24 hours to ensure all the PLA granule was dissolved. PALF fibres were coated with the PLA solutions using an in-house pre-pregger machine and left overnight at room temperature to dry. PLA solution was also cast onto the glass panel to produce a thin film. Both PLA film and pre-pregs were then dried under vacuum for further 24 hours to ensure the complete removal of the solvent. The weight of the initial PALF and PALF/PLA pre-preg was measured to determine the amount of the PLA in each pre-preg. The aligned PALF/PLA pre-pregs and PLA thin film were layered in a 150 mm x 80mm x 3 mm mould and were compressed moulded at 175 °C to produce unidirectional composites (Figure 1b). The fabrication method has been described in detail in our previous study [14]. In this study, composites containing 40 wt. % and 60 wt. % PALF are used.

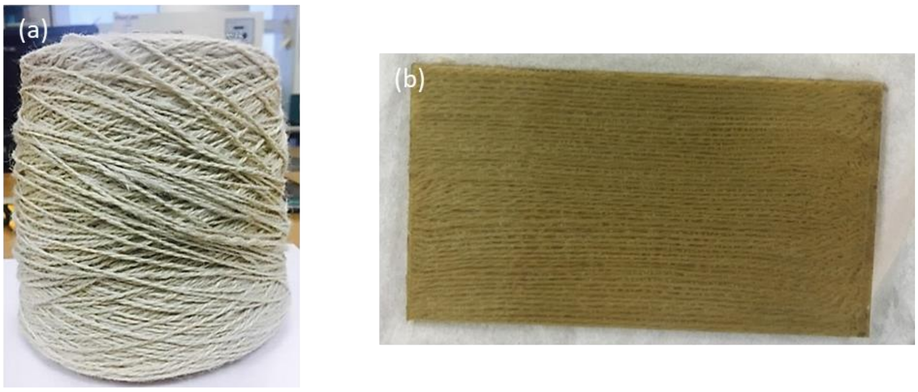

Fig. 1. (a) pineapple leaf fibre yarn, (b) unidirectional PALF/PLA composite

2.3 Moisture Absorption

The neat PLA and PALF/PLA composites were conditioned at 60°C until they reached a constant weight. The specimens then were exposed to high humidity (90% RH) of H_2O solution at elevated temperature (50°C) in a humidity chamber (Malvern, USA). The weight was measured at each interval time for the duration of up to 30 days. The percentage of moisture uptake was computed by using Eq. (1)

$$\text{Moisture uptake (\%)} = \frac{W_a\text{-}W_b}{W_b} \times 100 \quad (1)$$

2.4 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis was used to measure changes in the weight loss while heating was carried out using a Mettler Toledo SDTA 851 analyser (Columbus, United State). The sample was heated in a programmed temperature range of 25 ℃ to 800 ℃ using a heating rate of 10 ℃ per minute in an inert atmosphere with nitrogen flow.

2.4 Differential Scanning Calorimetry (DSC)

The DSC analysis was carried out in a temperature range of 30 and 220℃ using a heating and cooling rate of 10°C/min using a TA- Q200 machine. The non-aged and ageing samples were heated under a nitrogen flow at a rate of 50 mL/min. The percentage crystallinity of PLA was determined by using Eq. (2)

$$\text{Percentage pf Crystallinity (Xc)} = \frac{\Delta H_m}{\Delta H_{m100}} \times 100\% \quad (2)$$

where ΔH_m is the melting enthalpy of the sample, the theoretical enthalpy of melting for 100% crystalline PLA (ΔH_{m100}) = 93.7 J/g. The crystallinity of PLA in PALF/PLA was estimated using Eq. (3) where W is the weight fraction of PLA in the biocomposites fibres [14].

$$\text{Crystallinity (Xc)} = \frac{\Delta H_m}{\Delta H_{m100(1\text{-}wf)}} \times 100\% \quad (3)$$

3. Results

3.1 Moisture Absorption

The biodegradable PLA even though is hydrophobic, they are humidity sensitive at a higher temperature and may induce a higher hydrolysis rate. Natural fibre, being hydrophilic is susceptible to water absorption and may swell causing dimensional changes to the composite upon exposure to water or moisture. The percentage of the moisture adsorbed by neat PLA and PALF/PLA composites as a function of time when exposure to moisture at 50°C and 90% RH is shown in Figure 2. In general, all the specimens tend to absorb moisture in a humid environment. It can be seen that neat PLA, being hydrophobic materials absorb very little moisture and very gradually in the first 6 days of exposure time, approximately 0.62% possibly through micro-voids form in the PLA during fabrication. This slow absorption is sustained up to 18 days before a small increase of 1.93% at the end of 30 days of exposure time. This small increase in water uptake after 18 days of the exposure is probably due to the formation of cracks or pores in the neat PLA specimens as a result of hydrolytic degradation which further facilitates the water absorption [12]. It was also observed that the rate of moisture absorption for the neat PLA in this study is higher than those carried out at room temperature [15,16] suggesting that PLA may undergo faster hydrolytic degradation at elevated temperature and humidity compared to room temperature [12].

With the addition of 40 wt. % of the PALF fibre, the composite absorbed the moisture rapidly in the first week of the exposure, a 290% significantly than the neat PLA. After that, the rate of absorption is stable till the end of exposure time (2.84%). When higher fibre loading is used (60 wt.% PALF), the composite absorbed a significant amount of moisture in the first 6 days of exposure time and showed a maximum moisture absorption (7.51%) after 30 days of exposure. The moisture absorption pattern of the composite showed a Fickian behaviour. In natural fibre reinforced polymer composite, water transportation is facilitated by the matrix/fibre interfaces through capillary mechanism [17]. Therefore, composite with a higher amount of the hydrophilic phases will have a higher initial absorption rate as shown in the first week of the exposure period. Afterwards, the equilibrium moisture absorption is reached as their moisture content is almost constant with time. During this period, the structural damage of the PALF may give extra space for moisture absorption [18, 19].

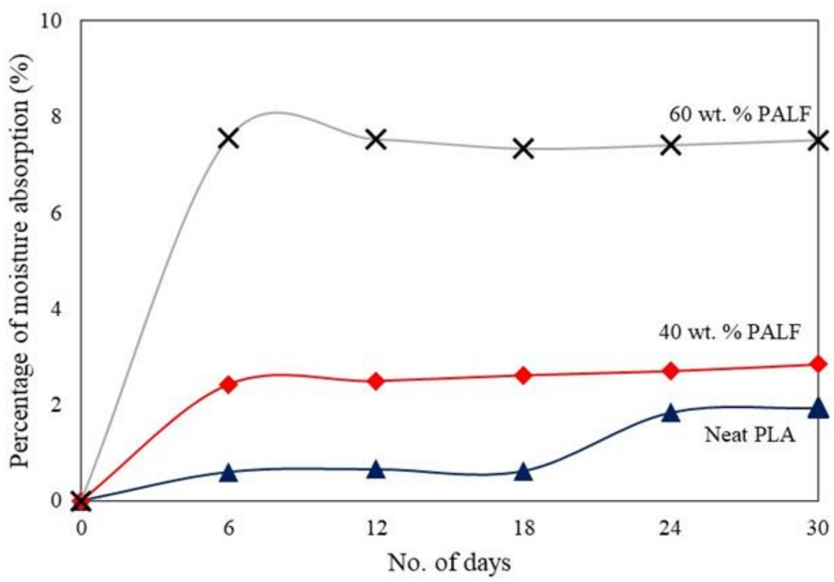

Fig. 2. Moisture absorption for neat PLA and PALF/PLA composites as a function of conditioning time

3.2 Thermogravimetric Analysis

The thermal stability of the neat PLA, PALF and PALF/PLA composites was carried out by TGA analysis and shown in Figure 3. Typically, natural fibre will have three stages of thermal decomposition where major weight loss occurs; 50-100°C due to moisture evaporation that presents in fibre [9]. The thermal degradation of PALF fibre, which occurred at 263°C led to rapid weight loss until it reached 392°C. This stage is related to the thermal decomposition of the hemicellulose and cellulose structures [20, 21]. PLA, on the other hand, is thermally stable up to 300° C, before it experiences a fast weight loss in a single step between 300 and 400°C. The residue obtained at the end of the test was 0.15%. It can be seen that the presence of the PALF reduced the thermal stability of the PLA. The onset degradation for 40 wt. % PALF was reduced to about 60°C than the neat PLA. However, it may be noticed that with the increase of the PALF content to 60 wt. %, the onset degradation temperature is not significantly altered and occurred at the same temperature (approximately 270°C). Thus, the composites may be produced without the risk of heat damage inside the machine because the PLA processing temperature used is around 175°C. At this temperature, the composites are reinforced with 40 wt. % PALF, for example, retained more than 96 % of its weight. As a result, no deterioration is expected to happen during the short fabrication process.

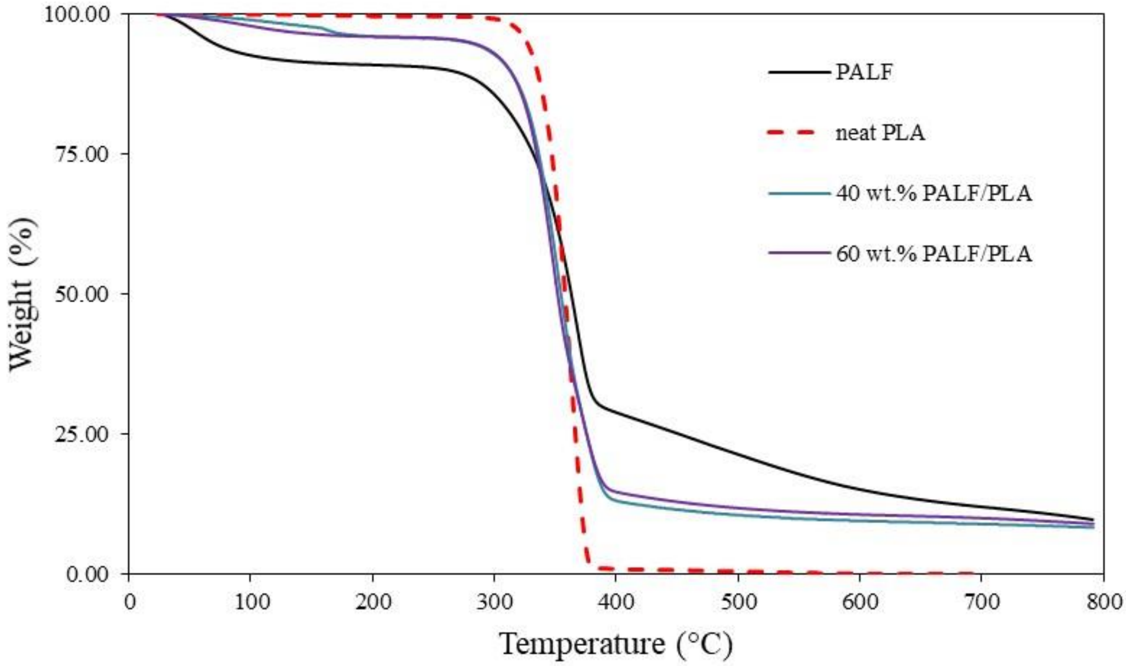

Fig. 3. TGA of PLA, PALF and PALF/PLA composites with different fibre loadings

3.3 Differential Scanning Calorimetry

When a semi-crystalline polymer like PLA is exposed to high temperatures and moisture, the amorphous portions are susceptible to hydrolysis and may alter their initial thermal characteristic. The DSC traces of the neat PLA, PALF and PALF/PLA before and after conditioning is shown in Figure 4 and Table 1.

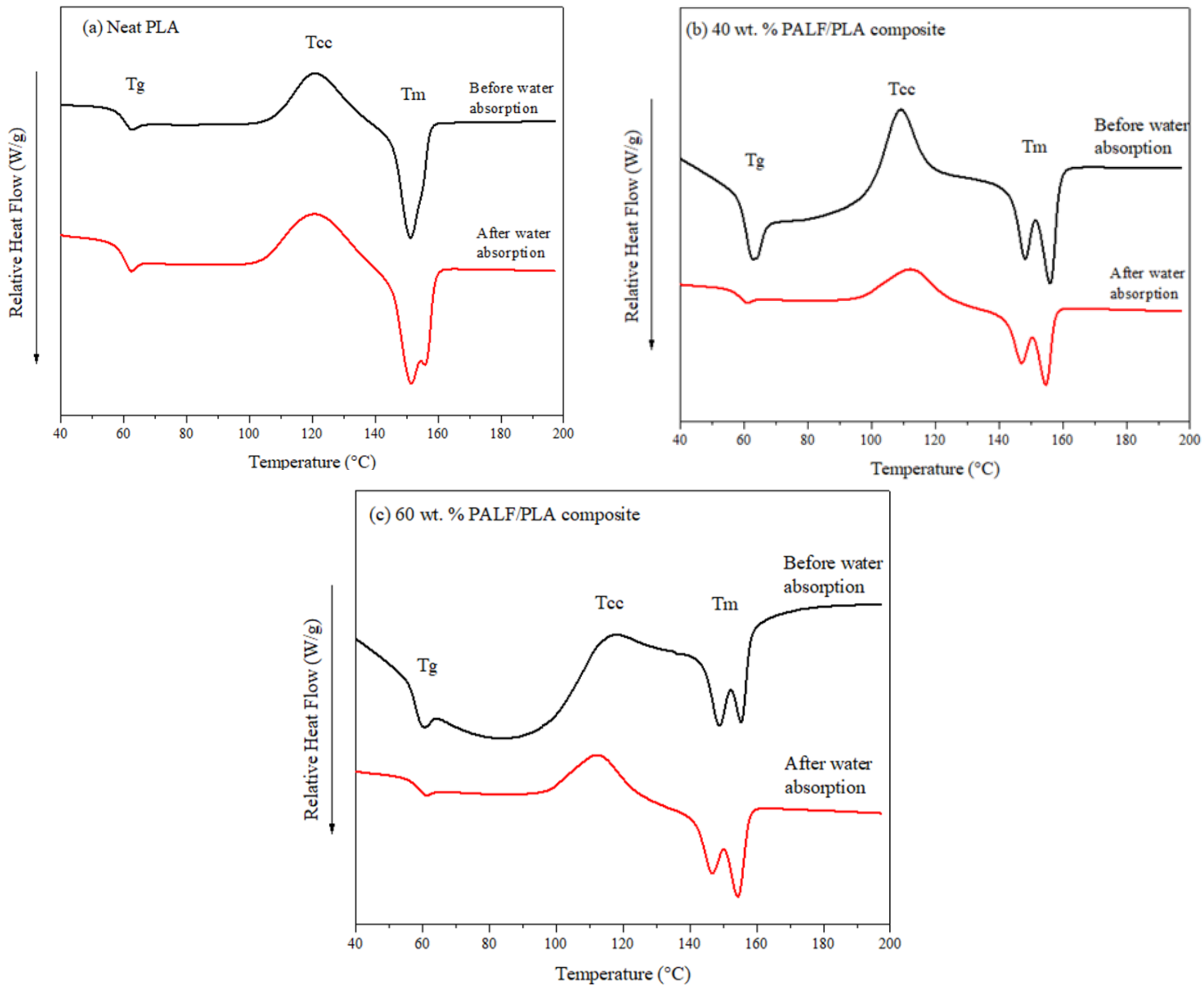

Fig. 4. DSC curve of neat PLA and PALF/ PLA composites before and after 30 days conditioned at 50°C with 90% RH

Table 1
Thermal characteristics of neat PLA and PLA reinforced PALF composites before and after 30 days conditioned at 50°C with 90% RH

Conditions	Fibre Loading (wt. %)	Tg (°C)	Tm (J/g)	Xc (%)
Unaged	Neat PLA	59.28	151.39	27.41
	40	60.28	149.71	28.61
	60	59.43	149.45	24.82
Aged	Neat PLA	46.03	144.08	34.42
	40	50.97	147.93	32.39
	60	56.24	143.56	30.81

When polymers are exposed to increased humidity and temperature, the spherulitic growth rate, crystal interphase, and lamellar thickness are expected to change as a result of the free energy changes that occur during crystal formation [12]. After conditioning, the neat PLA show a decrease in glass transition temperature (Tg) and the presence of bimodal melting (Tm) after the conditioning. The PALF/PLA composite experience similar changes in their thermal characteristic. The reduction of the Tg could be due to the plasticizing of the amorphous phase by the absorbed water. Jamshidi *et al.,* [20] associate the decrease of the Tg of PLA with the reduction of its molecular weight due to hydrolysis suggesting cleavage of the chain at the –C–O– ester group by water molecules. The PLA chain becomes shortened and more mobile thus resulting in a decrease in the Tg [3].

For both PLA and PALF/PLA composite, there is only a slight shifting observed in melting temperature after 30 days of exposure time. Their degree of crystallinity increased after the exposure. This might be due to the rearrangement of the amorphous PLA segments into the crystalline phase through chain scissions during the hydrolysis of PLA, known as chemi-crystallisation [12,23]. Micro-cracking that formed in the matrix due to fibre swelling may also facilitate water penetration into the composite and PLA region [23], which further plasticises the PLA and as a consequence, increase the PLA crystallinity. Double melting endotherms for PLA and its composites are present after ageing possibly resulting from the melting of crystalline structure domains that contain different sizes. This suggests there is a rearrangement of the polymer chain(s) orientation and morphology that occurred due to the reduction of the molecular weight during the hydrolytic degradation process [4,24].

4. Conclusions

The aligned and unidirectional PALF/ PLA composite was fabricated by using pre-pregging and hot compression moulding. The effect of the fibre addition on the moisture absorption and thermal properties of composites were studied after exposure to high humidity at elevated temperature. The moisture absorption behaviour in PALF/PLA followed the Fickian Law and increase with the increase of the fibre loadings. The composite achieved optimum moisture absorption at the end of 30-day conditions, possibly due to the hydrophilic nature of the PALF fibre. The presence of the PALF in the composite reduces the initial thermal degradation of the neat PLA approximately by 60°C. The DSC analysis showed that the Tg of the neat PLA did not change with the addition of the PALF. However, upon exposure to the high humidity and high temperature, all the samples experienced a reduction in their Tg and shifting of Tm to the lower temperature while the value of their crystallinity has been increased. This indicates that hydrolytic degradation has set in, particularly in the amorphous region of the semi-crystalline PLA polymer. The alteration of the thermal properties of the PALF/PLA due to the hygrothermal ageing exposure may have significant consequences on their mechanical performance. Thus, comprehensive mechanical testing is needed to properly quantify the deleterious effect of the moisture and elevated temperature on the PALF/PLA to diverse their application and prevent failure.

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References
[1] Sheikh Md Fadzullah, Siti Hajar, Zaleha Mustafa, Siti Nur Rabiatutadawiah Ramli, Qurratu'Aini Yaacob, and Ain Fatihah Mohamed Yusoff. "Preliminary study on the mechanical properties of continuous long pineapple leaf fibre reinforced PLA biocomposites." In *Key Engineering Materials*, vol. 694, pp. 18-22. Trans Tech Publications Ltd, 2016. https://doi.org/10.4028/www.scientific.net/KEM.694.18

[2] Getme, Abhijit Sudamrao, and Brijesh Patel. "A review: bio-fiber's as reinforcement in composites of polylactic acid (PLA)." *Materials Today: Proceedings* 26 (2020): 2116-2122. https://doi.org/10.1016/j.matpr.2020.02.457

[3] Yu, Tao, Fei Sun, Minyu Lu, and Yan Li. "Water absorption and hygrothermal aging behavior of short ramie fiber-reinforced poly (lactic acid) composites." *Polymer Composites* 39, no. 4 (2018): 1098-1104. https://doi.org/10.1002/pc.24038

[4] Tham, Wei Ling, Beng Teik Poh, Zainal Arifin Mohd Ishak, and Wen Shyang Chow. "Characterisation of water absorption of biodegradable poly (lactic acid)/halloysite nanotube nanocomposites at different temperatures." *Journal of Engineering Science* 12 (2016): 13.
[5] Ilyas, Rushdan Ahmad, Salit Mohd Sapuan, Mohamad Ridzwan Ishak, and Edi Syams Zainudin. "Water transport properties of bio-nanocomposites reinforced by sugar palm (Arenga Pinnata) nanofibrillated cellulose." *Journal of Advanced Research in Fluid Mechanics and Thermal Sciences Journal* 51, no. 2 (2018): 234-246.
[6] Asim, Mohammad, Mohammad Jawaid, Khalina Abdan, and Mohamad Ridzwan Ishak. "Effect of alkali and silane treatments on mechanical and fibre-matrix bond strength of kenaf and pineapple leaf fibres." *Journal of Bionic Engineering* 13, no. 3 (2016): 426-435. https://doi.org/10.1016/S1672-6529(16)60315-3
[7] Fadzullah, SH Sheikh Md, and Zaleha Mustafa. "Fabrication and processing of pineapple leaf fiber reinforced composites." In *Green approaches to biocomposite materials science and engineering*, pp. 125-147. IGI Global, 2016. https://doi.org/10.4018/978-1-5225-0424-5.ch006
[8] Huda, Masud S., Lawrence T. Drzal, Amar K. Mohanty, and Manjusri Misra. "Effect of chemical modifications of the pineapple leaf fiber surfaces on the interfacial and mechanical properties of laminated biocomposites." *Composite Interfaces* 15, no. 2-3 (2008): 169-191. https://doi.org/10.1163/156855408783810920
[9] Zainudin, Amira Syuhada, and Abdul Rahim Othman. "Thermal Stability of PALF-PP and PALF-PLA for Natural Fiber Honeycomb Core Materials." *Journal of Advanced Research in Fluid Mechanics and Thermal Sciences* 87, no. 1 (2021): 20-29. https://doi.org/10.37934/arfmts.87.1.2029
[10] Thyavihalli Girijappa, Yashas Gowda, Sanjay Mavinkere Rangappa, Jyotishkumar Parameswaranpillai, and Suchart Siengchin. "Natural fibers as sustainable and renewable resource for development of eco-friendly composites: a comprehensive review." *Frontiers in Materials* 6 (2019): 226. https://doi.org/10.3389/fmats.2019.00226
[11] Harris, Angela M., and Ellen C. Lee. "Heat and humidity performance of injection molded PLA for durable applications." *Journal of Applied Polymer Science* 115, no. 3 (2010): 1380-1389. https://doi.org/10.1002/app.30815
[12] Muthuraj, Rajendran, Manjusri Misra, and A. K. Mohanty. "Hydrolytic degradation of biodegradable polyesters under simulated environmental conditions." *Journal of Applied Polymer Science* 132, no. 27 (2015): 1-13. https://doi.org/10.1002/app.42189
[13] Ramli, Siti Nur Rabiatutadawiah, Siti Hajar Sheikh Md Fadzullah, and Zaleha Mustafa. "The effect of alkaline treatment and fiber length on pineapple leaf fiber reinforced poly lactic acid biocomposites." *Jurnal Teknologi* 79, no. 5-2 (2017): 111-115. https://doi.org/10.11113/jt.v79.11293
[14] Mustafa, Zaleha, Anira Shahidah Razali, Siti Hajar Sheikh Md Fadzullah, Sivakumar Dhar Malingam, Aslina Anjang, Qumrul Ahsan, and Thanate Ratanawilai. "Fabrication of aligned pineapple leaf fibre reinforced polylactic acid composite for high performance biocomposites." *Malaysian Journal of Microscopy* 18, no. 1 (2022): 99-106.
[15] Razali, Anira Shahidah, Zaleha Mustafa, Azizah Shaaban, Siti Hajar Sheikh Md Fadzullah, Zurina Shamsudin, Toibah Abd Rahim, and Aslina Anjang. "Mechanical degradation of pineapple leaf fibre reinforced polylactic acid green composite due to hydrolysis exposure." *Proceedings of Mechanical Engineering Research Day 2018* (2018): 239-240.
[16] Zaaba, Nor Fasihah, and Mariatti Jaafar. "A review on degradation mechanisms of polylactic acid: Hydrolytic, photodegradative, microbial, and enzymatic degradation." *Polymer Engineering & Science* 60, no. 9 (2020): 2061-2075. https://doi.org/10.1002/pen.25511
[17] Azwa, Z. N., B. F. Yousif, A. C. Manalo, and W. Karunasena. "A review on the degradability of polymeric composites based on natural fibres." *Materials & Design* 47 (2013): 424-442. https://doi.org/10.1016/j.matdes.2012.11.025
[18] Zulkafli, Norizzati, Sivakumar Dhar Malingam, Siti Hajar Sheikh Md Fadzullah, Zaleha Mustafa, Kamarul Ariffin Zakaria, and Sivaraos Subramonian. "Effect of water absorption on the mechanical properties of cross-ply hybrid pseudo-stem banana/glass fibre reinforced polypropylene composite." *Materials Research Express* 6, no. 9 (2019): 095326. https://doi.org/10.1088/2053-1591/ab3203
[19] Cai, Ming, Xian Zhang, Baozhong Sun, Hitoshi Takagi, Geoffrey IN Waterhouse, and Yan Li. "Durable mechanical properties of unidirectional flax fiber/phenolic composites under hydrothermal aging." *Composites Science and Technology* (2022): 109264. https://doi.org/10.1016/j.compscitech.2022.109264
[20] Espinach, F. X., S. Boufi, M. Delgado-Aguilar, F. Julián, P. Mutjé, and J. A. Méndez. "Composites from poly (lactic acid) and bleached chemical fibres: Thermal properties." *Composites Part B: Engineering* 134 (2018): 169-176. https://doi.org/10.1016/j.compositesb.2017.09.055
[21] Sunny, Tom, Kim L. Pickering, and Shen Hin Lim. "Alkali treatment of hemp fibres for the production of aligned hemp fibre mats for composite reinforcement." *Cellulose* 27, no. 5 (2020): 2569-2582. https://doi.org/10.1007/s10570-019-02939-3
[22] Jamshidi, K., S-H. Hyon, and Y. Ikada. "Thermal characterization of polylactides." *Polymer* 29, no. 12 (1988): 2229-2234. https://doi.org/10.1016/0032-3861(88)90116-4

[23] Islam, Mohammad Saiful, Kim L. Pickering, and Nic J. Foreman. "Influence of hygrothermal ageing on the physico-mechanical properties of alkali treated industrial hemp fibre reinforced polylactic acid composites." *Journal of Polymers and the Environment* 18, no. 4 (2010): 696-704. https://doi.org/10.1007/s10924-010-0225-9

[24] Zhang, Xiaoqing, Maria Espiritu, Alex Bilyk, and Lusiana Kurniawan. "Morphological behaviour of poly (lactic acid) during hydrolytic degradation." *Polymer Degradation and Stability* 93, no. 10 (2008): 1964-1970. https://doi.org/10.1016/j.polymdegradstab.2008.06.007