WATER ABSORPTION BEHAVIOUR AND ITS EFFECT ON MECHANICAL AND THERMAL PROPERTIES OF CONTINUOUS UNIDIRECTIONAL PINEAPPLE LEAF FIBRE REINFORCED POLY LACTIC ACID COMPOSITES

Z. Mustafa[1*], A.S. Razali[1], A.A.A. Sappa[2], S.H.S.M. Fadzullah[3], S.D. Malingam[2] and T. Ratanawilai[4]

[1]Faculty of Manufacturing Engineering,
Universiti Teknikal Malaysia Melaka, Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, Malaysia.

[2]Faculty of Engineering,
Universiti Malaysia Sabah, 88400 Kota Kinabalu,
Sabah, Malaysia.

[3]Fakulti Kejuruteraan Mekanikal,
Universiti Teknikal Malaysia Melaka, Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, Malaysia.

Department of Industrial and Manufacturing Engineering, Faculty of Engineering, Prince of Songkla University, Hat Yai, 90112,
Songkhla, Thailand.

*Corresponding Author's Email: zaleha@utem.edu.my

Article History: Received 18 December 2022; Revised 6 July 2023; Accepted 2 August 2023

ABSTRACT: Pineapple leaf fibre (PALF) is hydrophilic material and prone to humidity absorption. The present moisture may alter the initial properties of natural fibre-based composite and it became more deleterious when using high fibre content. The objective of this paper investigates the water absorption behaviour and its effects on the mechanical and thermal properties of unidirectional PALF-reinforced polylactic acid (PLA) composites. The PLA composites with high content fibre (40 to 80 wt.%) of aligned PALF were prepared using a novel method combining pre-pregging and compression moulding followed by water immersion for 43 days. Composites showed significant saturation weight gains and diffusion coefficients than neat PLA, which increased from 0.46 to 19.22 cm^2/s indicating that the presence of PALF

fibre induced higher water absorption due to their hydrophilic nature. The initial tensile strength of the composites is up to 213.0 MPa, approximately 500% higher than neat PLA (33.56 MPa). The composite shows significant degradation up to 64 % and 68% in tensile and modulus after the ageing process and is influenced by the PALF fibre contents. Morphology analysis shows the presence of micro-cracks and voids due to the degradation of PLA and debonding of PALF and PLA after ageing. Crystalline contents of the materials increased up to 33% due to hydrolysis upon exposure to the water.

KEYWORDS: *Natural Fibre; Fibre Loadings; Water Absorption; Pineapple Leaf Fibres; Polylactic acid; Mechanical and Thermal Properties*

1.0 INTRODUCTION

Polylactic acid (PLA), a biodegradable thermoplastic polymer has great potential as an eco-material due to its high strength and modulus has not been for its brittleness, which limits its applications [1, 2]. Thus, the PLA is often blended with other polymers as well as reinforced with fibres and fillers to improve their brittleness [3]. Incorporation of the natural fibres as reinforcements in composites such as pineapple leaf fibre, sisal, banana, jute, oil palm, pineapple, kenaf and coir has been shown to improve the mechanical properties of the PLA [4-8]. Natural fibres possess attractive traits as they are cheap, have low density, have high specific strength and modulus, are abundantly available, are CO_2 neutrality as well as renewable engineering materials [1, 3, 9-11].

Pineapple leaf fibres (PALF) stand out among popular natural fibres due to their outstanding mechanical properties, thanks to their remarkable composition of high cellulose (70-82%), lignin (5-12%), and ash (1.1%). This unique composition also contributes to PALF being a fibre with a relatively low microfibrillar angle [11, 12]. Nonetheless, as a lignocellulosic fibre containing hydroxyl groups, natural fibres suffer from a notable limitation—high vulnerability to moisture absorption and insufficient interfacial bonding with hydrophobic thermoplastic matrices. The absorption of water can significantly impact the behaviour of organic materials, leading to alterations in their chemical and physical characteristics and consequently affecting their mechanical and thermal properties [1, 13-16]. Normally, the incorporation of a high amount of natural fibre in the composite is often required to produce high strength composite. Therefore, the rate of mechanical degradation due to moisture will become more significant with the increase in fibre content. However, there is a scarcity of

published data regarding the detrimental impact of moisture on PALF-based composites when they are manufactured with high fibre content. Therefore, the primary objective of this paper is to comprehensively assess the substantial effects of water absorption on the mechanical and thermal properties of composites incorporating natural fibres (PALF), particularly under high fibre loading conditions. The aim is to ascertain the composite's resilience in practical applications.

2.0 MATERIALS AND METHODS

2.1 Materials

PLA grade 6100D purchased from Nature Works, USA with a 1.25 g/cm^3 density was used as the matrix material. For reinforcement, PALF was employed in the form of a two-ply yarn, obtained from Mechasolve Sdn. Bhd, Malaysia. The yarn had a diameter of less than 15 mm, with a density of 1.526 g/cm^3 and a tex number of 640.00 g/km.

2.2 Sample Preparation

The raw PALF underwent an alkaline treatment using a 5 wt% NaOH solution, following the procedure described in [5]. The composite uses a novel method combining pre-pregging and compression moulding PALF as reported in our previous work [4]. To determine their fibre content as per the required percentages (40, 60, 80 wt. %), the fibres and pre-pregs were weighed both before and after impregnation. Subsequently, the material was subjected to hot compression moulding using a Carver machine from the USA. The process took place in a mould with dimensions of 150 × 80 × 3 mm (length, width, and thickness) at a temperature of 175 °C and under a pressure of 15 tonnes. Afterwards, the moulded specimen was rapidly cooled to room temperature by quenching it with water. The sample was then cut following ASTM D3039 for tensile testing.

2.3 Water Absorption and Dimensional Stability

Water absorption (WA) and thickness swelling (TS) were determined according to ASTM D570-88. Five specimens from each fibre loading with dimensions of 150 mm × 20 mm × 3 mm were immersed in a distilled water bath at 27 °C for 43 days with their weight periodically measured at a 1-week interval. The WA and TS were calculated using

$$WA(\%) = \left(\frac{W_t - W_0}{W_0} \right) \times 100\% \quad (1)$$

where W_0 is the initial weight, and W_t is the wet weight of the specimen at a time, t.

$$TS(\%) = \left(\frac{T_t - T_0}{T_0} \right) \times 100\% \quad (2)$$

where T_0 is the initial thickness, and T_t is the wet thickness, both at the given time, t. The diffusibility of the composite was analysed using the Fickian mechanism. The diffusion coefficient (D) is calculated using [13]

$$D = \pi \left[\frac{mT}{4M_\infty} \right]^2 \quad (3)$$

where M_∞ is equilibrium water uptake, m is the slope of the linear portion of the sorption curve of M_t versus $t^{1/2}$ and T is the initial thickness of the sample.

2.4 Thermal Analysis

A Perkin Elmer DSC thermal analyser was utilized to perform thermal analysis in the temperature range of 30 to 200 °C. The heating rate employed was 10 °C/min, and the analysis was conducted under a pure nitrogen gas atmosphere. Key parameters such as the glass transition temperature (Tg), melt temperature (Tm), cold crystallization temperature (Tcc), and heat of melting (ΔHm) were determined. The percentage crystallinity was calculated using Equation (4).

$$X_c(\%) = \frac{\Delta H_m - \Delta H_c}{w \Delta H_m^0} \times 100 \quad (4)$$

In the equation, ΔH_m represents the heat of melting, ΔHc is cold crystallization ΔH^0_m denotes the heat of melting for a 100% crystalline PLA sample (considered as $\Delta H^0_m = 93.1$ J/g), and w is the weight fraction of PLA in the analysed sample [1].

2.5 Mechanical Testing

The tensile test was carried out using 20 kN Shimadzu Universal Testing AGS-X, Japan at a 2 mm/min speed rate and a gauge length of 50 mm. Five specimens were tested for each fibre loading, before and after the water immersion test.

2.6 Morphological Analysis

The fracture surface was analysed using a Carl Zeiss EVO 50 scanning electron microscope manufactured at an accelerating voltage of 10 kV. The composite fractured surfaces were coated with gold using a mini sputter coater before the test.

3.0 RESULTS AND DISCUSSION

3.1 Water Absorption and Physical Properties

Figure 1 illustrates the water uptake behaviour of neat PLA and its composites. Initially, a linear relationship between water uptake and time is observed for all samples, followed by a saturation plateau, indicating typical Fickian behaviour. Neat PLA exhibits slow water absorption until it reaches a saturation point of 0.02% after 43 days of immersion. This minimal water absorption can be attributed to the hydrophobic nature of neat PLA. The addition of PALF into the PLA matrix, led to higher water uptake value due to the hydrophilic nature of the lignocellulosic fibres, similarly as reported [14]. A rapid water uptake was observed in the first few days with a linear relationship between the M_∞ and $t^{1/2}$ for all fibre loadings. The composite with higher fibre loading took a longer time to reach saturation point. At 40 wt% PALF/PLA, the water intake activity reached a plateau after 21 days of immersion time, while for 80 wt%, the sample reached a plateau after 30 days.

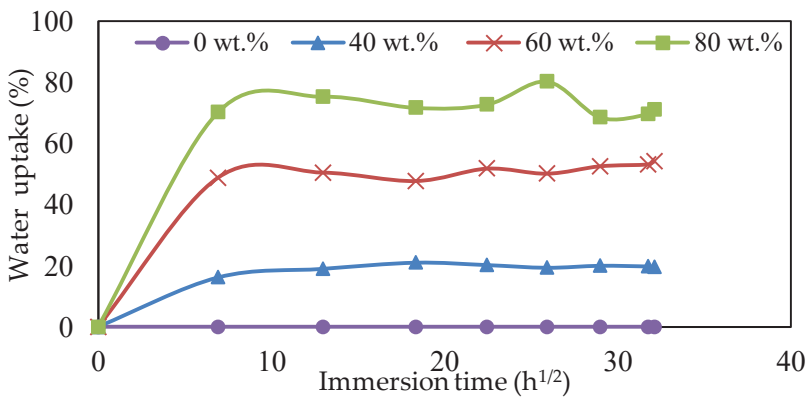


Figure 1: Water absorption for neat PLA and PALF/PLA composites

Table 1 presents the saturation water absorption value and diffusion coefficient of neat PLA and its composites. As the fibre content increases, the values of D (diffusion coefficient) and M∞ (saturation water absorption value) also increase due to the higher cellulose content in the composites, resulting in greater water absorption. The samples were machined on the sides thus exposing the fibres along all four sides, allowing water ingress through capillaries and causing fibre swelling. Thus, a higher fibre content increases the surface exposure for water diffusion, leading to greater water intake. These findings are consistent with previous studies [15-17]. The swelling of the fibres may reduce the strength of the fibre-matrix interface by relieving stress caused by the increased fibre dimensions. In general, the composites achieve optimal water absorption after 28 days of immersion. Subsequently, a significant weight loss is observed after 43 days of degradation study (Figure 2), possibly due to PLA leaching out, particularly facilitated at the fibre/matrix interface. This effect becomes more pronounced at higher fibre loading, as evident in the morphology analysis (Figures 5(d) and 5(f)). These findings align with previous research [18-19].

Table 1: Maximum moisture content (M∞), diffusion coefficient (D) of PLA and PALF/PLA composites

Fibre Loading (wt%)	M_∞ (%)	m (% /sec$^{1/2}$)	D x 10^{-8} (cm^2/s)
0	0.02	0.00001	0.48
40	16.55	0.02821	5.76
60	62.11	0.13370	9.08
80	80.38	0.22990	19.22

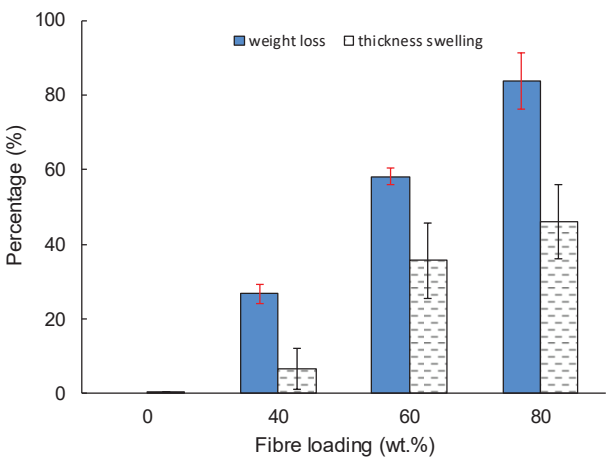
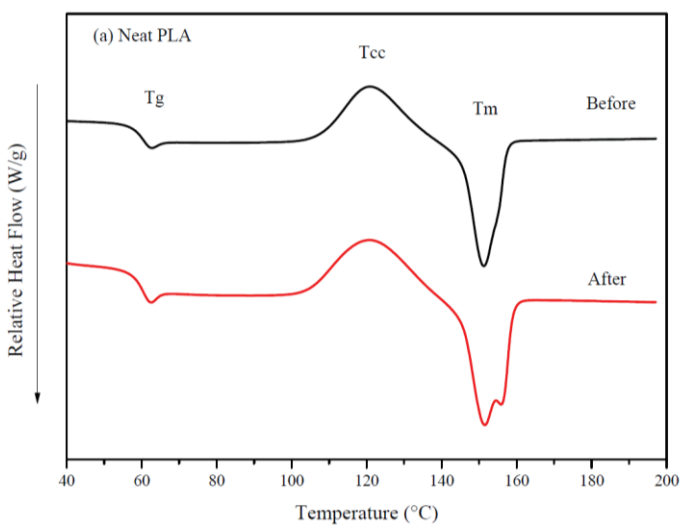


Figure 2: Percentage of thickness swelling and weight loss for neat PLA and PALF/PLA composites after 43 days in water immersion

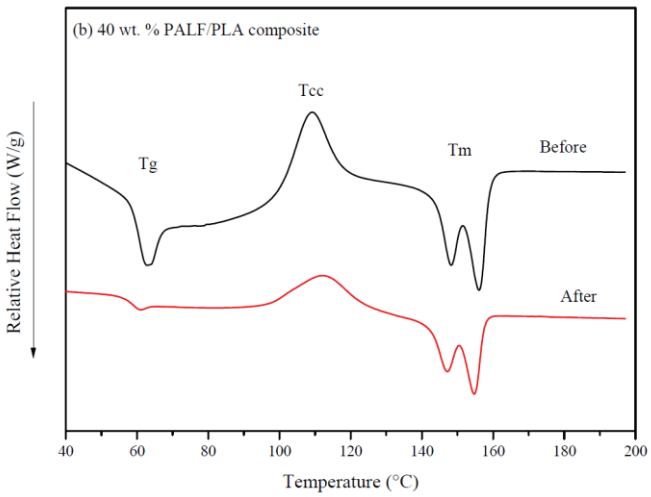
3.2 Thermal Properties

Thermal analysis shows a reduction in T_g for neat PLA and its composite after ageing (Figure 3). This effect may be attributed to either a decrease in the molecular weight or the scissoring of molecular chain lengths of PALF, along with the shortening of PLA chains during hydrolysis. Consequently, the mobility of the molecules increases, resulting in a lower Tg [1].

While no significant change in the T_m of the neat PLA and its composites, their degree of crystallinity increased from 27% to 31% for neat PLA. In the PALF/PLA composites, an increase in crystallinity was observed, from 28% to 34% for 40 wt% PALF and from 24% to 33% for 60 wt% PALF, respectively. This phenomenon can be attributed to the rearrangement of amorphous PLA segments into a crystalline phase through chain scissions during PLA hydrolysis, referred to as chemi-crystallization, as reported in [15]. Notably, the amount of crystallinity remained consistent after water immersion, regardless of the PALF loadings. After the ageing process, both PLA and its composites exhibit double melting endotherms, likely indicating the melting of crystalline structure domains with different sizes. This observation suggests a rearrangement in polymer chain orientation and morphology, which can be attributed to the reduction of molecular weight during the hydrolytic degradation process. These findings align with similar observations reported in previous studies [19-20].



(a)



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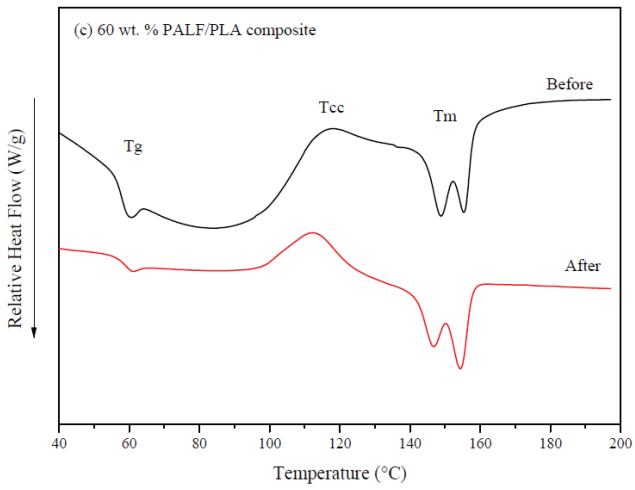


(c)

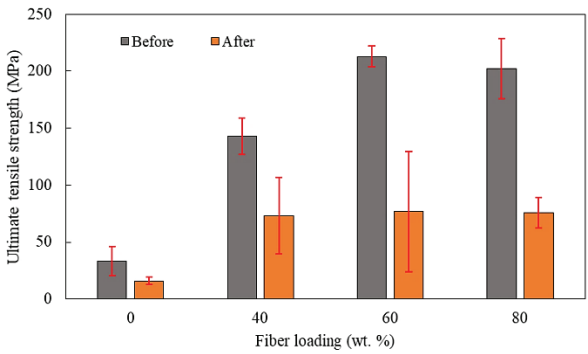
Figure 3: DSC curve of (a) neat PLA (b) 40 wt% and (c) 60 wt% PALF/ PLA composites before and after 43 days in water immersion

3.3 Mechanical Properties

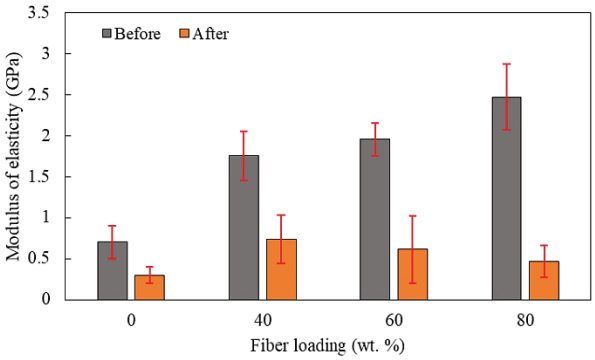
The change of the mechanical properties due to water absorptivity for different fibre loading is shown in Figure 4 with their morphological observation in Figure 5. In general, the exposure to water resulted in a decline in the tensile properties of the neat PLA and PALF/PLA composites. The initial strength and modulus of the unaged neat PLA are 33.56 MPa and 0.7 GPa respectively (Figure 4(a) and (b)). The polymer failed in a brittle-like manner with low strain (Figure 4(c)) which is typical for brittle material (Figure 5(a)). After water

immersion, the tensile strength and modulus were reduced to 15.95 MPa and 0.3 GPa respectively. The hydrolysis degradation of PLA caused plasticization and swelling of neat PLA chains that could increase their toughness and consequently outweigh the effect of the increased crystallinity resulting in the decrease of the modulus, similarly as reported in [15, 21].

The addition of the PALF fibre significantly enhances the unaged composite properties with the optimum tensile strength of PALF/PLA achieved at 60 wt.% of fibre (213.00 MPa) (Figure 4(a). The fracture surface of the composite showed broken fibres were still embedded in the resin together with some cavities left by pulled-out fibres with no apparent fibre debonding (Figure 5(c)). The total morphology indicates that effective load transfers have taken place which led to the highest strength observed among all composites. The composite was prepared using the pre-pregging technique where the individual yarn was impregnated with matrix solution. This will reduce the travelling distance of the melting matrix onto the fibre during hot compression moulding later, thus allowing better penetration around the fibre, effective interface bonding and reinforcement are then achieved (Figures 5(c) and 5(e)) even at high fibre loading and might contribute to the significant improvement in their tensile properties. This finding agrees with previous studies [8, 9].



(a)



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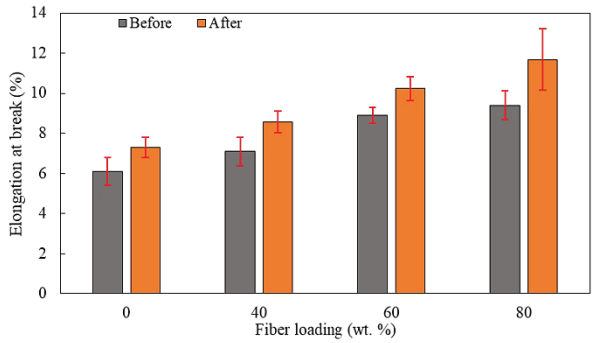

(c)

Figure 4: Effect of the water immersion on tensile (a) strength; (b) modulus and (c) strain at break of neat PLA and PALF/PLA composites

However, the initial mechanical properties of the composite significantly altered after moisture exposure. The tensile strength and modulus of 40wt.% PALF/PLA composite was reduced from 143.20 MPa and 1.75 GPa to 73.33 MPa and 740 MPa, respectively. This mechanical degradation is more significant as the fibre loading increases. At 60 wt.% PALF loading, the tensile strength and modulus of the composite severely degraded from 213.0 MPa and 2.47 GPa to 76.92 MPa and 0.61 GPa respectively. As the water uptake increased with fibre loading, the wicking of water would swell the fibre. The different expansion and contraction experienced by PALF and PLA might lead to the loss of interfacial adhesion and weakening of the integrity of the composites, as reported in [1, 15]. The fracture surface of aged 40 wt% PALF composite (Figure 5(d)) showed fibre pulls-out with interface debonding which might contribute to degradation of their tensile strength. As the fibre loading increased, more apparent damage is observed with the fibre surface appearing rougher and more split yarn resulting in exposure of fine fibrils (Figure 5(f)). At the same time, it was also observed that in all aged specimens the tensile strain

values increase after the immersion test (Figure 4(c)). In neat PLA, their fracture surface changed from typical brittle fracture facets with a river-like pattern (Figure 5(a)) to fading river-like patterns with an increase of plasticization resulting in higher tensile strain (Figure 5(b)).

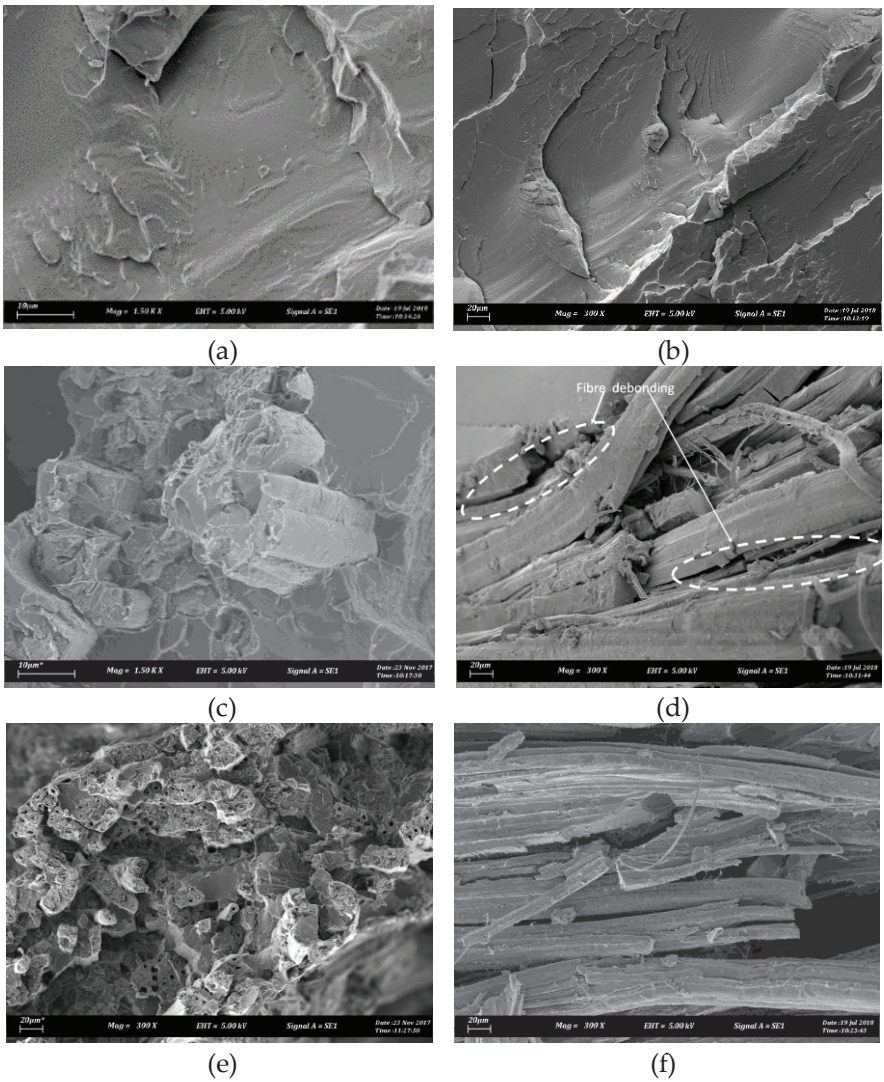

Figure 5. The fracture surface of (a) unaged neat PLA (b) aged neat PLA (c) dry 40 wt% (d) aged 40 wt% (e) unaged 60 wt% and (f) aged 60 wt% PALF/PLA composites

For 40 wt.% PALF composites, the strain increased by 20% while at 80 wt.% PALF composites, their strain increased up to 24%. Twisting and splitting of yarn into thinners fibrils is more apparent with increased PALF loading (Figures 5(d) and 5(f)) as the result of large deformation

of tensile strain in aged samples. This could be due to the softening and plasticising effect of water on both PLA and the plant fibre, similarly as described in [22].

4.0 CONCLUSION

Following 43 days of water immersion, the PALF/PLA composites experienced a substantial decrease in their initial tensile strength and modulus, losing up to 64% and 68% respectively. Additionally, an increase in crystallinity up to 33% was observed possibly due to the hydrolysis process. The notable degradation of the initial mechanical properties emphasizes the need to protect the composite interface when applying hydrophobic materials, in order to prevent premature failure caused by moisture absorption during applications.

ACKNOWLEDGMENTS

The authors acknowledge the financial support from the Universiti Teknikal Malaysia Melaka through a short-term grant (PJP/2023/TD/FKP/S01975) and the use of their laboratory and equipment.

AUTHOR CONTRIBUTIONS

Z. Mustafa: Validation, Writing-Reviewing and Editing, Supervision, Funding acquisition; A.S. Razali: Methodology, Writing- Original Draft Preparation, Data curation; A.A.A. Sappa: Data curation; S.H.S.M. Fadzullah: Validation, Writing-Reviewing, Funding acquisition; S.D. Malingam: Writing-Reviewing; T. Ratanawilai: Writing-Reviewing

CONFLICTS OF INTEREST

The manuscript has not been published elsewhere and is not under consideration by other journals. All authors have approved the review, agree with its submission and declare no conflict of interest in the manuscript.

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