IOP Conf. Series: Materials Science and Engineering **368** (2018) 012035 doi:10.1088/1757-899X/368/1/012035

The effects of alkali treatment on the mechanical and chemical properties of pineapple leaf fibres (PALF) and adhesion to epoxy resin

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Abstract. The focus of this study was to obtain the optimum alkaline treatment for pineapple leaf fibre and its effect on the mechanical and chemical properties, surface topography, heat resistivity, as well as its interfacial bonding with epoxy matrix. There were 6 different treatment conditions set for the fibre. The morphology of a single fibre observed under the Digital Image Analyzer indicates slight reduction in fibre diameter with increasing NaOH concentration. The Scanning Electron Microscope (SEM) results show the deteriorating effect of alkali, which can be seen from the removal of impurities and increase in surface roughness. The mechanical analysis indicates that 6% NaOH treatment with 3-hour immersion period yielded the highest tensile strength. The adhesion between single fibre and epoxy resin was analysed through the micro-droplet test. Alkaline treatment results in better mechanical bonding between fibre and epoxy resin. It was found that 6% NaOH treatment with 1-hour immersion yielded highest interfacial shear stress. However, as NaOH concentration went above 6 %, the fibre started to show reduction in mechanical properties, as well as fibre-matrix interlocking. The TGA analysis implies that alkaline treatment improved the thermal stability and heat resistivity of the fibre.

1. Introduction

Natural fibre has gained growing interest and usage over the recent years due to their potential capability as a substituent for synthetic fibres. Natural fibres possess valuable properties such as low density and high specific strength and stiffness [1]. Besides economical reason, natural fibres are a renewable resource, for which production requires little energy, with CO_2 absorption, and returning oxygen to the environment [2].

There are numerous research being carried out previously on natural fibre reinforced composite (NFRC) [3]. When talking about NFRC, it is crucial to understand the chemical composition and surface adhesive bonding between matrix and reinforcement that affect the mechanical properties of the composite. Natural fibres are known for their hydrophilic polar characteristic, which is against the non-polar hydrophobic matrix properties [4]. This condition lead to weak mechanical bonding between the matrix and reinforcement, resulting in poor mechanical properties of the composite produced.

Hydrophilic nature of natural fibre requires chemical modification to improve interfacial properties between fibre and resin [5]. One of the most economical and conservative chemical modification methods is alkali treatment. Alkaline treatment increases surface roughness, as well as the amount of exposed cellulose on the fibre surface by eliminating cellulosic content that covers the external surface of the fibre cell wall [6], resulting in better mechanical interlocking.

Previous works have recorded numerous trials involving alkali treatment for natural fibres. Atiqah et al. [7] treated kenaf fibre with 6% sodium hydroxide (NaOH) solution for 3 hours and showed optimum results for flexural, tensile and impact strengths. Claudia Merlini et al. [8] attempted alkaline treatment on banana short fibres with 10% NaOH solution for 1 hourPanyasart et. al [9] treated pineapple leaf fibre (PALF) with 5% NaOH solution and 5 hours immersion period at room temperature. Previous work by Asim et. al [4] on alkali treatment for pineapple fibre showed increase in mechanical properties for fibres treated with 6% NaOH. The alkaline treatments showed improved behaviour in mechanical properties as compared to untreated fibres. The objective of this study was to obtain the optimum alkaline treatment for pineapple leaf single fibre strand and its effect on the mechanical properties, surface micrography, heat resistivity, as well as interfacial bonding with epoxy matrix.

2. Materials

The Pineapple Leaf Fibre (PALF) was obtained from Johor, Malaysia. Properties of pineapple leaf fibre [10] is shown in Table 1:

Table 1. Properties of Pineapple Leaf Fibre (PALF)

Properties	PALF
Density (g/cm^3)	1.07
Tensile strength (MPa)	126.60
Elongation at break (%)	2.2
Young's modulus (MPa)	4405

The chemical used in this research is Sodium Hydroxide (NaOH) pellet. For resin system, epoxy DM15 made of Bisphenol A was selected, with low molecular weight and high mechanical strength. The resin was made of 2 parts; Part A (base) and Part B (hardener). The ratio between base and hardener is shown as follow:

$$\text{DM15 (Part A)}: \text{DM15 (Part B)} = 5:1 \qquad (1)$$

2.1 Alkali Treatment

The PALF fibres were immersed in NaOH with various treatment concentration; 4%, 6% and 8% (w/v) as illustrated in Table 2:

Table 2. NaOH treatment condition on PALF

Sample	NaOH %	Duration (Hours)	Abbreviation
Untreated	0	0	Untreated
4% + 1 hour	4	1	4%1h
4% + 3 hour	4	3	4%3h
6% + 1 hour	6	1	6%1h
6% + 3 hour	6	3	6%3h
8% + 1 hour	8	1	8%1h
8% + 3 hour	8	3	8%3h

The alkaline treatment involved dissolving NaOH pellet according to the designated concentration, as performed previously by [11]. For instance, to make 4% NaOH solution, 40g NaOH pellet was dissolved in 1 litre of distilled water. PALF fibres were cut to about 400mm, and immersed in the NaOH solution accordingly, followed by rinse off using distilled water. pH paper was used to check alkalinity by immersing it in the solution. The fibres were washed until pH 7 was obtained. Last step of the alkaline treatment was oven drying, at 60°C for 24 hours.

2.2 Characterizations

2.2.1 Physical Analysis. The PALF fibre's diameter was measured under Olympus SZX 12-CCD Digital Image Analyzer at 20 times magnification. The average diameter of 5 different points was taken for each fibre strand. For each type of concentration, 10 samples were prepared and averaged.

2.2.2 Morphology Analysis. The surface morphology of the fibre was observed under Hitachi S-3400N Scanning Electron Microscope (SEM) with the setting of 5.0 kV magnification between 300 to 800 times.

2.2.3 Single Fibre Tensile Test. Single fibre tensile test was conducted as per ASTM D3822 using Instron 3365 Dual Column Table Top Universal Testing Systems with 5kN maximum load at the rate of 2 mm/min. The single fibre was attached to a paper holder, as illustrated in Figure 1.

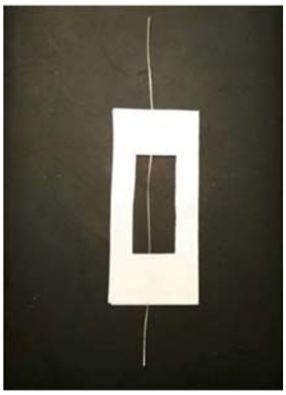

Figure 1. PALF single fibre attached to paper holder

The sample was attached to the gripper, and average of 10 samples were taken for each combination of NaOH treatment.

2.2.4 Adhesion to Epoxy Resin. The micro-droplet test was carried out to investigate the adhesive bonding between PALF fibre and epoxy resin. The technique was based on previous work of Dai et. al, (2011), whereby resin was wetted onto the single PALF fibre that was attached to a paper holder to form a micro-droplet surrounding the fibre diameter due to surface tension. The embedded length of the micro-droplet was observed under a digital image analyser. The schematic of the micro-droplet test is shown in Figure 2.

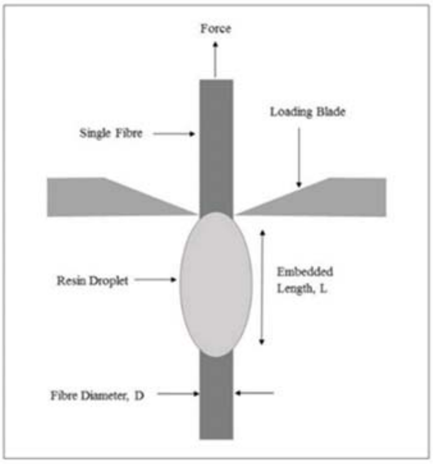

Figure 2. The schematic of the micro-droplet test

The figure illustrated vertical arrangement of the micro droplet test. The top part of the paper holder was clamped to the gripper. While the fibre being pulled upwards, the resin droplet was hold by the loading blade, opposing the pulling direction. The interfacial shear stress (IFSS) was calculated as follow:

$$\tau = \frac{F}{\pi DL} \quad (2)$$

Where F is the maximum load, D is the fibre diameter, and L is the embedded length. Average of 10 samples per NaOH combination was taken for record. The tensile test was conducted with 5kN maximum load and at a rate of 0.1 mm/min.

2.2.5 Thermal Stability Analysis. The thermogravimetric analysis (TGA) was conducted to investigate thermal behaviour of PALF fibre with a temperature setting between 30 °C up to 600 °C at a rate of 10 °C/min.

3.0 Results and Discussion

3.1 Physical Analysis
The effect of alkaline treatment on single fibre diameter is shown in Table 3:

Table 3. Effect of alkalization on PALF single fibre diameter

Treatment conditions	Diameter (mm)	Std Dev
Untreated	0.070	0.024
4%1h	0.107	0.029
4%3h	0.070	0.009
6%1h	0.102	0.023
6%3h	0.121	0.014
8%1h	0.115	0.047
8%3h	0.096	0.016

In general, there is a variation in fibre diameter throughout the range of different NaOH concentration and period treatment. Average diameter of untreated PALF fibre is 0.070 ± 0.024 mm, which is in accordance with the finding by previous researcher [12]. From the result, the diameter of single strand fibre increased after the alkaline treatment. This is because, the treatment caused the fibres to clumped together, made it difficult to be segregated into single fibre strand, unlike the untreated fibre. In terms of the aspect ratio, the result will be normalised for tensile test as the calculation will consider the fibre diameter with respect to the force needed to break the fibre. Looking at the trend, treatment beyond 6% of NaOH concentration yielded in reduction of fibre diameter. This could correspond to removal of waxy epidermal tissue, as also reported by previous researcher [2].

3.2 Morphology Analysis
Figure 3, 4 and 5 showed the effect of alkaline treatment on surface morphology of the PALF fibre.

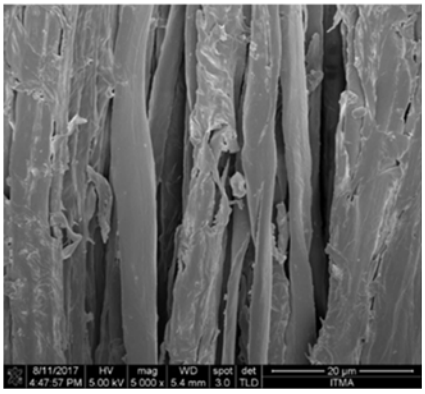

Figure 3. SEM micro-graph for untreated fibre.

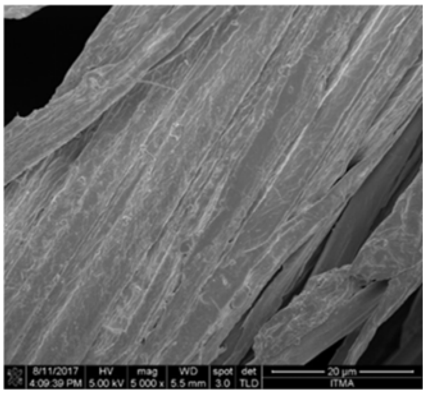

Figure 4.. SEM micro-graph for fibre treated with 6% NaOH for 4 hours

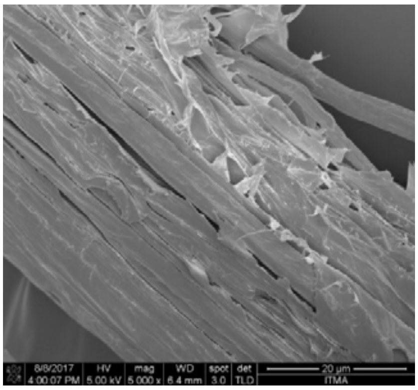

Figure 5. SEM micro-graph for fibre treated with 8% NaOH for 4 hours.

Figure 3 illustrated the untreated PALF whereby considerable deposits of impurities could be seen on the surface. As also mentioned by previous researcher, the impurities existed on fibre surface caused poor fibre-matrix interfacial adhesion due to limited area of contact between fibre and matrix [13]. Figure x showed the surface of PALF fibre treated with 4% NaOH. It can be seen that impurities have been removed, making the surface cleaner and rougher. Damages on the fibre are observable on a few spots. The removal of waxy layer, impurities and elements such as lignin and hemicellulose due to alkaline treatment contribute to better surface adhesion between the fibre and epoxy resin, as also depicted by previous study [11]. This is illustrated in Figure 4 whereby the fibre surface is cleaner due to removal of impurities.

However, as NaOH concentration further increased, damages on the surface became more severe, due to corrosive effect of the alkaline solution, as shown in Figure 5. Excessive delignification caused fibre deterioration, hence making fibre weak and reduce its mechanical properties. The micrograph result is in line with the tensile test finding explained in section 3.3.

3.3 Single Fibre Tensile Test

Figure 6 presents the average Ultimate Tensile Strength of PALF single fibre.

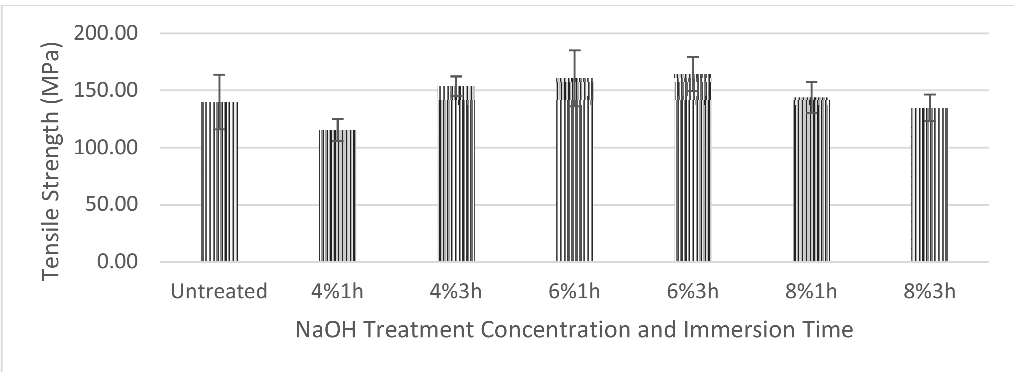

Figure 6. PALF single fibre tensile strength with different NaOH concentration

The untreated fibre recorded tensile strength of 139.90 MPa, which is in accordance with previous findings [10]. The alkali treatment resulted in increasing trend of the tensile strength properties, until the optimum point is reached. The highest tensile strength recorded was 164.55 MPa, corresponding to NaOH treatment with 6% concentration and 3 hours immersion time. This is equivalent to 18% increment as compared to the untreated fibre. As the NaOH concentration went higher to 8%, the tensile strength of PALF single fibre started to show decreasing pattern. This could be due to excessive removal of waxy layers and lignin of the fibre in high alkaline concentration, resulting in weaker or damaged fibre. Similar finding was also reported by previous researcher [13]. This can be proven from morphology presented in Figure 5.

3.4 Adhesion Analysis to Epoxy Resin

The interfacial shear strength for untreated and treated PALF with epoxy resin is presented in Figure 7.

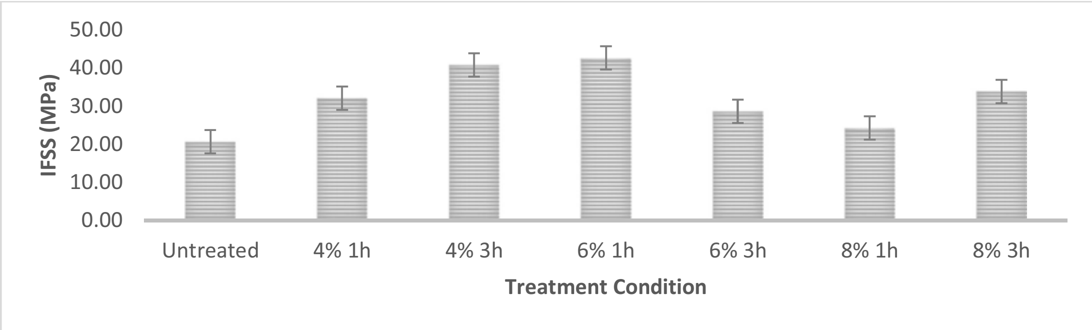

Figure 7. The interfacial shear strength for untreated and treated PALF with epoxy resin

The interfacial shear strength (IFSS) denoted the adhesive interlocking between single fibre and epoxy resin droplet. Higher IFSS means greater force is needed to detach the resin droplet from fibre surface. The untreated fibre recorded the IFSS of 20.64 MPa. The IFSS improved with alkali treatment. The peak was recorded at 42.67 MPa, corresponded with 6% NaOH concentration and 1 hour soaking period. This is equivalent to 106% improvement compared to untreated fibre. Alkali treatment removed natural and artificial impurities, which resulted in increase in surface roughness, hence leading to better interlocking adhesion and greater amount of exposed cellulose on the fibre surface. Similar finding was obtained by previous researcher [14]. Rougher surface enabled better fibre wetting through increased number of possible reaction sites. The effect of rough surface is evident in morphology analysis in Figure 4.

3.5 Thermal Stability Analysis

Figure 8 illustrate the thermogravimetric analysis (TGA) for both treated and untreated PALF single fibre.

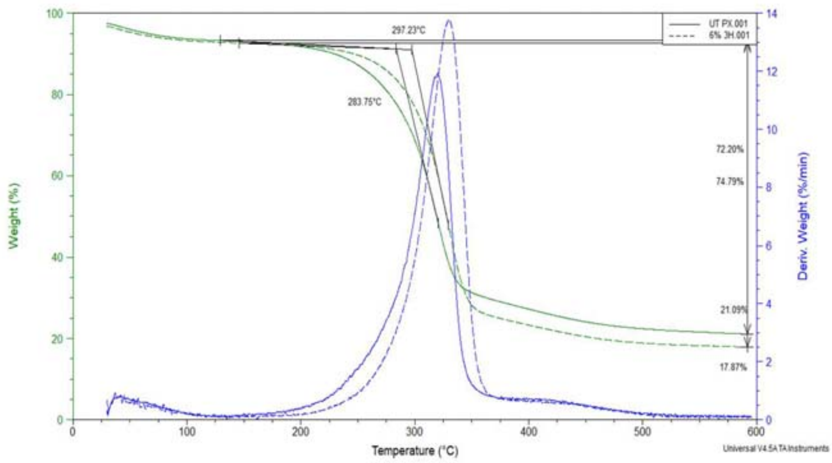

Figure 8. Thermal stability behaviour for untreated and treated PALF

From figure 8, untreated PALF fibre started to lose weight earlier than treated fibre. This is corresponding to removal of water content of untreated fibre, whereby the presence of hemicellulose lead to higher moisture absorption of the fibre [15].

At temperature 80°C, moisture started to evaporate from the sample. [16] depicted that due to hydrophilic property of natural fibre, it is impossible to completely remove moisture from the sample. The decomposition temperature for untreated fibre started at 283.75°C, whilst for the treated fibre, temperature increased by 4.75% to 297.23°C.

From a practical standpoint, the onset of a massive weight loss indicated thermal stability of the fibre. As shown in Figure 8, the onset temperature refers to sharp downward inclination in the TG curve. The untreated sample recorded 71.75% mass decomposition while the treated fibre was higher by 2.71%. The amount of residue left after the samples were degraded is reflected by the percentage of weight reduction at 500°C. The treated PALF fibre showed lower residue than untreated fibre. Some researcher depicted that this is due to the elimination of lignin component through alkalization. Lignin in natural fibre contributes to charring thus untreated fibre will have more char. The result obtained in this study is in line with previous studies [17].

The change in decomposition temperature, percentage decomposition and final weight are shown in Table 4.

Table 4. Thermal stability comparison between untreated and treated PALF

Treatment	Decomposition temperature (°C)	% Decomposition	% Final weight after decomposition
Untreated	282.25	71.75	21.05
4% 1h	296.52	76.79	16.49
4% 3h	298.1	74.68	17.14
6% 1h	308.34	80.52	12.83
6% 3h	296.57	74.46	17.83
8% 1h	302.16	81.01	13.22
8% 3h	300.54	76.85	15.51

The decomposition temperature indicated the starting temperature of burning the sample. The peak temperature for untreated fibre was recorded at 282.25°C. Meanwhile the treated fibre of 6% NaOH recorded higher decomposition temperature at 296.57°C. With alkalization, removal of hemicellulose component is predicted whereby the treated PALF fibre was initiated at higher temperature. As also mentioned by previous researcher [18], the reduction of hemicellulose and lignin from fibre treatment led to increase in thermal stability.

4. Conclusion

Based on the study, the optimum alkaline treatment for PALF is 6% NaOH concentration with 3-hour-hour immersion period, which resulted in 164.55 MPa tensile strength. However, for interfacial shear strength, the optimum NaOH concentration is 6 % with 1-hour soaking period, that yields the IFSS of 42.67 MPa. As the concentration increases to 8 %, the mechanical properties of PALF deteriorates by 18% down to 134.75 MPa. This could be due to excess delignification on fibre surface that contributed to the deteriorating effect. The SEM micrographs show that alkali treatment increases the surface roughness of the fibre, while the TGA results show that the treatment enhances the thermal stability of the fibre by an increase of 14.32 °C for the burning temperature.

Acknowledgement
This study was conducted in a collaborative laboratory known as the "Sustainable Aviation" - joint lab with Aerospace Malaysia Innovation Centre, Universiti Putra Malaysia and University of Nottingham Malaysia Campus, under Project no. BF-P06.

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