



STUDY OF PROPERTIES OF COCONUT FIBRE REINFORCED POLY (VINYL ALCOHOL) AS BIODEGRADABLE COMPOSITES

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ABSTRACT

Coconut fibre can be potentially used as one of the most crucial resources in the development of biodegradable polymer composites due to its excellent renewability and environmental friendliness. In this study, the coconut fibre was modified through alkali treatment (mercerization), and was integrated with poly(vinyl alcohol) (PVA) via solution casting method. The modified composites film produced was compared with the non-modified composites film in the aspect of tensile properties, hardness, thermal properties, morphology, as well as the moisture sensitivity. Besides, the effect of the composition of the treated and untreated fibre on the composites was investigated. Scanning electron microscopy (SEM) micrographs suggested that, the treated fibre which had better adhesion with the polymer matrix produced stronger composites. Tensile test results proved that the Young's modulus of the composites could be improved with the increase of fibre loading, and the enhancing effect was greater with the treated fibre. Hardness test showed that the increase of fibre increased the hardness, but high degree of alkalinity of the composites reduced its hardness. Thermogravimetric analysis (TGA) verified that the degradation temperature of the composites could be improved by increasing the filler content, but its thermal properties could be degraded with the presence of voids and pores in the matrix. Moisture experiment suggested that, the increment of treated fibre reduced the moisture sensitivity of the composites. Thus treated coconut fibre reinforced poly(vinyl alcohol) exhibited better properties than untreated fibre.

Keywords: coconut fibres, poly (vinyl alcohol), tensile testing, thermal property.

INTRODUCTION

In recent years, the drastic increment of plastics disposal due to the increasing global demand of non-renewable polymer products has resulted in the environmental destruction. Therefore, new environmental legislation and consumer pressure have encouraged the implementation of biodegradable natural fibre-reinforced polymer composites [1] as a substitution to the petroleum based polymers as well as the conventional non-renewable polymer composites.

Coconut fibre is one of the natural fibres abundantly available in tropical regions. According to official website of International Year for Natural Fibres 2009, approximately, 500 000 tonnes of coconut fibres are produced annually worldwide, mainly in India and Sri Lanka. Its total value is estimated at \$100 million. India and Sri Lanka are also the main exporters, followed by Thailand, Vietnam, the Philippines and Indonesia. Around half of the coconut fibres produced are exported in the form of raw fibre. Coconut fibre is extracted from the outer shell of a coconut. The common name, scientific name and plant family of coconut fibre is Coir, *Cocos nucifera* and Arecaceae (Palm), respectively [2]. Coconut fibre contains cellulose, hemicellulose and lignin as major composition as well as pectin, waxes and water. This non-wood fibre is extracted from the outer shell of a coconut by several methods, including retting as a traditional way, and decortication in which bacteria and fungi are used [3].

It has high specific strength and modulus, low density, reduced dermal and respiratory irritation, enhanced energy recovery, and low cost [4]. Coconut fibre is getting popular in the composites industries because of its outstanding biodegradability and environmental friendliness that outperform the conventional glass, carbon, basalt, and aramid.

Poly(vinyl alcohol) (PVA) is a water soluble synthetic polymer which is colorless and odorless. PVA has been considered to be a truly biodegradable synthetic polymer since 1930s. PVA has density of 1.19 g/cm³ and melting point of 180 °C [5]. This non-toxic polymer has high tensile strength and flexibility, good oxygen and aroma barrier properties, excellent emulsifying and adhesive properties [6], and high resistance to oil and grease [7]. It is widely used in papermaking, textiles, coatings, and as moisture barrier for dry food with inclusions [8]. Modification of PVA with various fillers is common to enhance its film performance. The dispersion state of fillers in this polymer is critical in determining the final property of the polymer composites.

Coconut fibres in general are hydrophilic in nature as they are derived from ligno-cellulose, which contain strongly polarized hydroxyl groups [9, 10]. These fibres, therefore, are less compatible with hydrophobic thermoplastics such as polyolefins and thermoset polymer matrices. Major limitations of using these fibres as reinforcements in such matrices include poor interfacial



adhesion between polar-hydrophilic fibre and nonpolar-hydrophobic matrix, and difficulties in mixing due to poor wetting of the fibre with the matrix. Besides, moisture absorption causes the swelling of fibre, leading to the microcracking and degradation of the composites [1]. Hence, physical and chemical treatments, such as silane treatment, benzoylation, styrene-acrylic emulsion, acetylation, bleaching, and mercerization are required to decrease the hydroxyl groups that involve in the hydrogen bonding within the cellulose molecules [11]. These treatments are able to introduce new moieties that improve the mechanical interlocking [12] and the adhesion between fibre and the matrix.

The ultimate aim of this study was to fabricate natural fibre reinforced polymer composites, by integrating PVA with treated and untreated coconut fibre, and to characterize the treated and untreated composites samples with SEM, TGA, tensile test, hardness test, and moisture absorption-desorption experiment. The effect of alkaline treatment and the filler loading on the properties of the polymer composites were investigated.

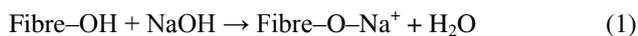
EXPERIMENTAL

Materials

Coconut fibre with density of 0.835 g/cm³ and average diameter of 0.2 mm was used as filler. PVA with a molecular weight (Mw) of 45,000-55,000, 87-89%, hydrolysed (CAS 9002-89-5) was obtained from R & M Chemicals Sdn. Bhd. Sodium hydroxide (NaOH), pellets (CAS 1310-73-2) of 40 g/mol for alkali treatment was supplied by R and M Chemicals Sdn. Bhd.

Alkali treatment of fibre

The coconut fibre (10 g) was cut into 5 mm and was soaked in distilled water at 70 °C for 1 h. The water was removed and the fibre was dried in the oven at 80 °C until constant weight. The NaOH (5 g) pellets were dissolved in distilled water (100 ml) and the solution was stirred. The dried fibre was soaked in the NaOH solution for 2 h. The reaction was illustrated in Eqn. (1). Finally, the fibre was removed from the solution, washed, and dried in the oven at 80 °C until constant weight [13].



Preparation of composites

Three types of composite samples were prepared: untreated composites, treated composites, and neat PVA. Both untreated and treated composites were prepared by mixing four different compositions of PVA with distilled water at a ratio of 1:10, in four beakers. The solutions were heated at 180 °C on a hot plate and were stirred until the PVA granules were completely dissolved. Four different compositions of fibres were added to the PVA

solution in the respective beakers, and were stirred until the fibres were evenly dispersed. Then, the solutions were poured into the petri dishes and dried in the oven at 70 °C for solidification. Lastly, the solids were hot pressed under required temperature and timer settings (Table-1) to produce composites films. The neat PVA sample was prepared with the same method as described above, for reference. Table-2 summarizes the composition of the samples prepared.

Characterization

Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) was used to evaluate the morphology of the fibre before and after treatment and the composites film. The fibre (5 mm long) and fractured surface of composites strip (10 mm x 10 mm x 1 mm³) were placed on the platforms and the fracture surfaces were observed under magnification range from 140x to 1200x and accelerating potential of 200 V to 30 kV.

Table-1. The setting of hot pressing technique.

Parameter	Condition
Temperature (°C)	185
Preheat time (min)	3
Venting time (min)	2
Full pressing cycle (min)	4
Cooling time (min)	3

Table-2. Composition of fibre and PVA in untreated composites, treated composites, and neat PVA.

Sample	PVA (wt%)	Fibre (wt%)
Neat PVA	100	0
5%	95	5
10%	90	10
15%	85	15
20%	80	20

Tensile test

Lloyd universal tensile machine was used to investigate the relationship between tensile strength and filler loading of the composites films. The sample (16 mm x 100 mm x 1 mm³) was tested with 5 mm/min cross speed, under ambient temperature. Before the experiment, all of the samples were kept dry in the oven at 60 °C to avoid the adverse effect of moisture content.



Thermogravimetric analysis

The thermal stability analysis of the polymer nanocomposites were carried out using Perkin Elmer Simultaneous Thermal Analyser 600 with temperature set between 30 to 800 °C with increment of 20 °C/min. The gas flow in the machine was N₂ at 20 ml/min from 25 to 700 °C and the gas was switched to O₂ from 700 to 800 °C. The sample size for thermal analysis was 7 mg. In this experiment, the change in the weight percentage of the composites film was determined as a function of increasing temperature.

Moisture Absorption-Desorption Test

In this experiment, the moisture sensitivities of different composites were determined. For moisture absorption test, the sample (10 mm x 10 mm x 1 mm³) was soaked in distilled water, and was weighed every 1 min until constant weight achieved. To study the moisture desorption characteristics, the same sample was dried in oven at 90 °C, and was weighed every 1 min until constant weight. Before the experiment, the samples were stored at room temperature with the same humidity level to ensure identical initial moisture content. The change in mass percentage of the sample during moisture intake and moisture release was calculated with Equation (2) [11].

$$\Delta M(t) = \frac{M_t - M_0}{M_0} \times 100 \quad (2)$$

where $\Delta M(t)$ is the change of mass percentage with respect to time, M_0 is the initial mass, and M_t is the instantaneous mass of moisture uptake and release.

RESULTS AND DISCUSSIONS

Morphology

Figure-1(a) and 1(b) show the SEM micrographs of untreated fibre and treated fibre. It was observed that the diameter of treated fibre was smaller, and the surface was rougher, compared with the untreated fibre. This was the result of alkali treatment, the process in which the minor constituents and impurities, such as pectin and waxes were removed by NaOH, leaving a number of pores on the surface of fibre [13].

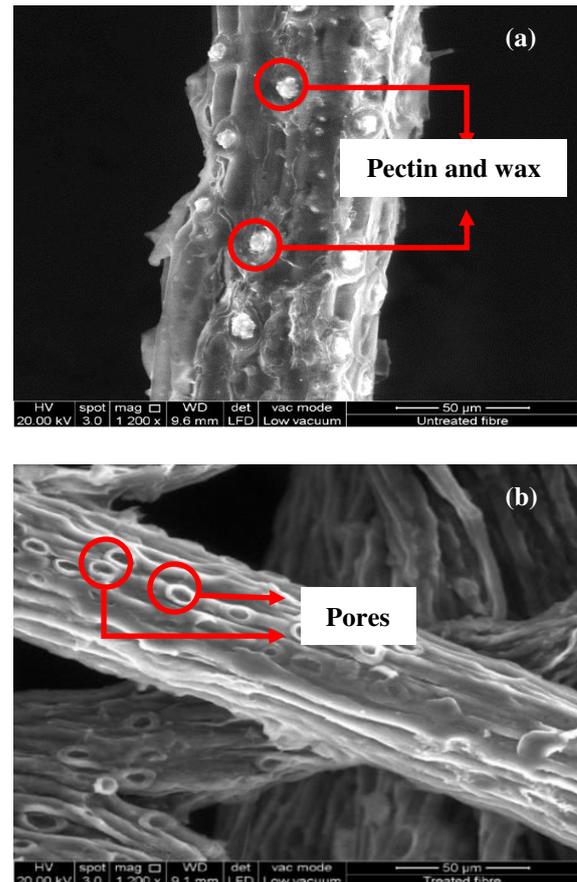
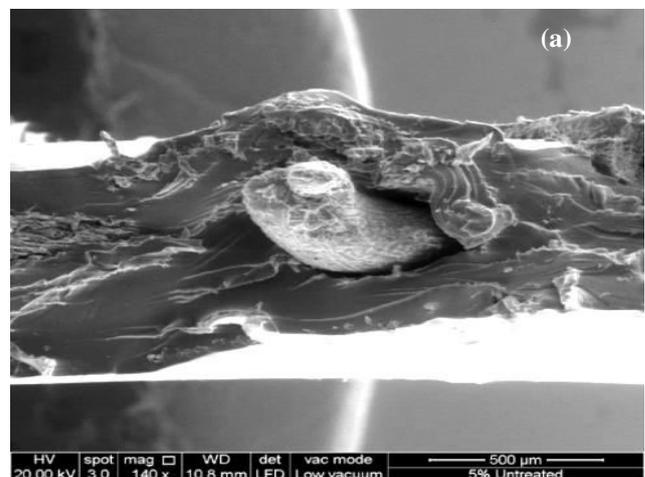


Figure-1. SEM images at 1200x magnification of (a) untreated and (b) treated fibre.

The fracture surfaces of untreated composites with filler content of 5% and 20% are displayed in Figure-2(a) and 2(b) respectively.



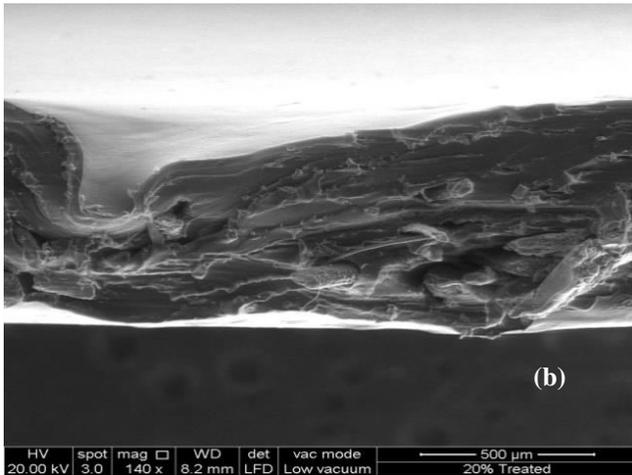


Figure-2. SEM images at 140x magnification of untreated composites with (a) 5% and (b) 20% of untreated coconut fibre.

More fibres were detected with increasing filler loading in the composites. The greatest amount of fibre was found in 20% fibre-PVA composites. For both 5% and 20% fibre-PVA composites, the fibre was either entirely or partially pulled out without breaking together with the matrix, indicating poor fibre-matrix adhesion. This was because the smooth surfaces and the impurities on the untreated fibre resulted in a small grabbing force between the fibre and the matrix [14].

Figure-3(a) and 3(b) show the fracture surfaces of treated composites with 5% and 20% filler, where there were more fibres found in 20% fibre-PVA composites.

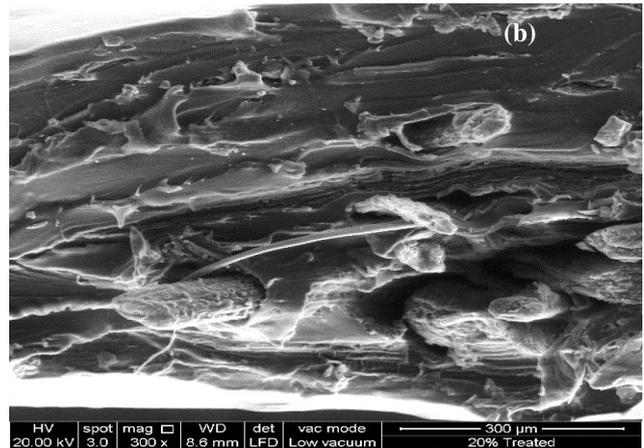
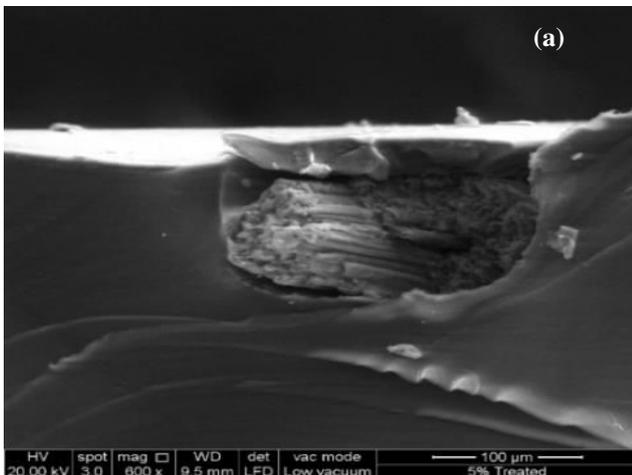


Figure-3. SEM images at 300x magnification of treated composites with (a) 5% and (b) 20% of untreated coconut fibre.

In 5% fibre-PVA composites, the fibre and matrix fractured together without being pulled out, illustrating a good adhesion between the fibre and the matrix. The rough and porous surfaces of treated fibre provided more chances of mechanical interlocking and surface interpenetration between the fibre and the matrix [12], leading to the improved mechanical properties.

For 5% and 20% untreated composites, as well as 20% treated composites, a number of voids and pores were observed on the surfaces of the matrix. This was attributed to the impaired composites fabricating process, whereby the stirring mechanism during the mixing of fibre and PVA solution caused the formation of air bubbles in the composites.

Tensile Test

Figure-4(a) shows the Young's modulus of untreated composites with different filler content. The modulus of composites increased with the increase of filler percentage, and reached the highest value at 20% fibre-PVA composites. With increasing fibre content, the interaction between the fibre and the matrix was enhanced, thus the crack propagation was inhibited [11]. In addition, the fibre functioned to scatter the external tensile stress throughout the composites, and hence the mechanical properties were improved.

The Young's modulus of treated composites with different filler percentage is displayed in Figure-4(b). The modulus increased with the increment of fibre. Besides, it was observed that the modulus of treated composites was greater than the modulus of untreated composites of the same filler percentage. Specifically in 5%, 10%, and 15%, the moduli of treated composites were improved by 26%, 34%, and 28% respectively. This indicated greater reinforcement effect on the mechanical properties of the treated composites. This was because the treated fibre acted as a nucleating agent that facilitated crystallization



in the polymer composites [14], as the rough surfaces of the treated fibre induced crystal formation. Besides, the interfacial connection and adhesion between the treated fibre and the matrix was stronger, as a result of the increased area of interpenetration [15]. Furthermore, the voids and defects found in the matrix due to the formation of bubbles also caused the untreated composites to have lower modulus than the treated composites, which was coherent with the SEM results.

However, the modulus decreased at 20% treated fibre-PVA composites, instead of having the highest value. This was caused by the presence of pores and voids that lowered the strength of the material, in accordance with the result in SEM micrographs. Besides, the great amount of fibre also resulted in the aggregation of fibre and the formation of agglomerates that conducted to the localized stress concentration of the composites [16], causing adverse effects on its mechanical properties.

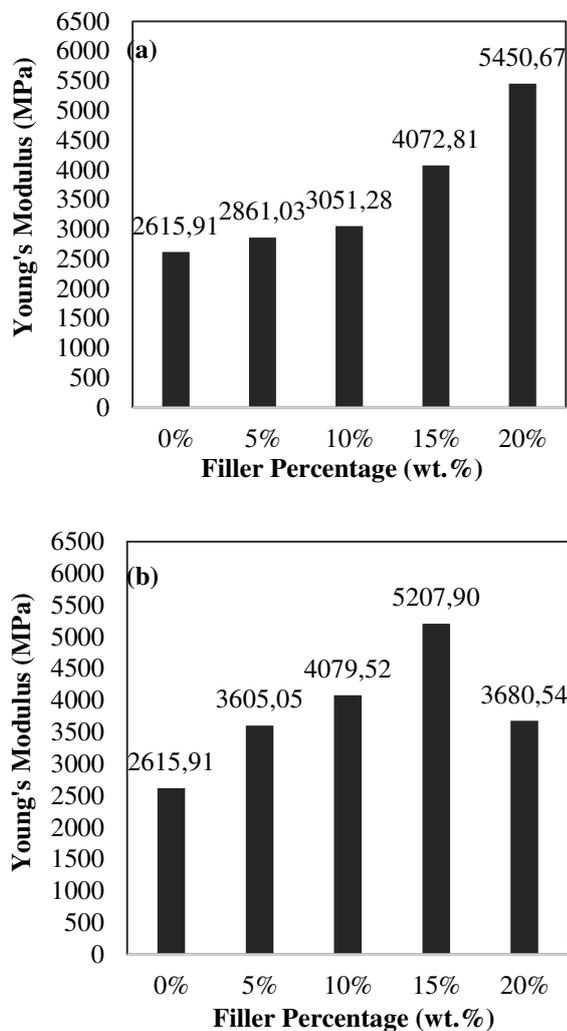


Figure-4. Young's modulus vs. filler percentage of (a) untreated and (b) treated composites film.

Hardness Test

Figure-5(a) shows the proportional relationship between the hardness of composites and the composition of untreated fibre. The hardness increased when the filler percentage increased. This was resulted from the dispersion of the compression force throughout the sample by the increasing number of fibre [14]. Moreover, the fibre that increased modulus of composites will also increase the hardness of the composites, because hardness is a function of the relative fibre volume and modulus [17].

Figure-5(b) shows the hardness of treated composites at different compositions of filler.

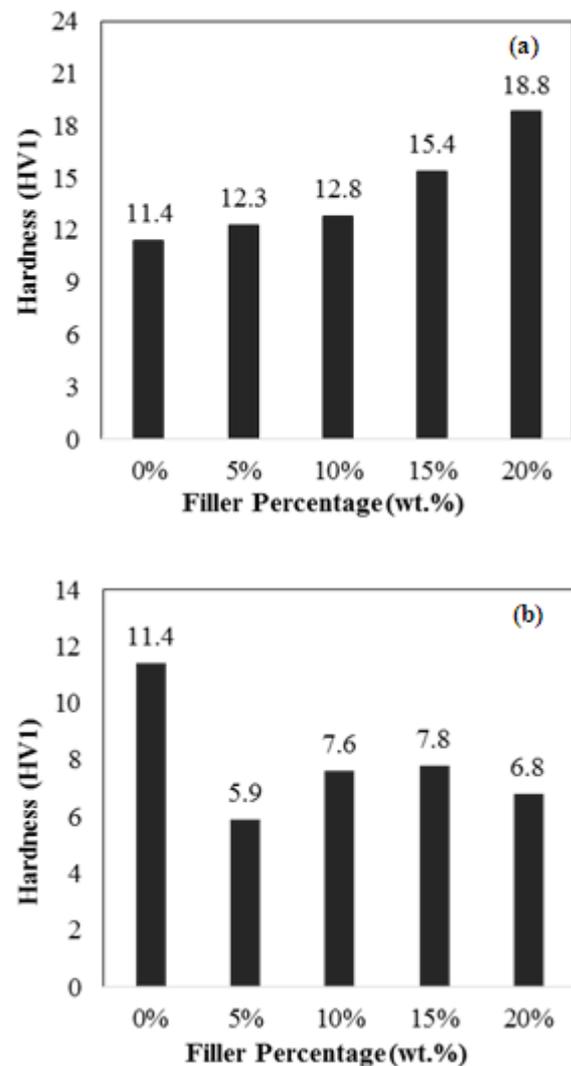


Figure-5. Hardness vs. filler percentage (a) untreated and (b) treated composites film.

It was discovered that, the hardness of all treated composites were lower than the hardness of untreated composites and pure PVA. This could be due to the incomplete removal of NaOH from the fibre during alkali treatment, whereby the excessive NaOH caused high alkalinity (high pH value) of the composites, which



conducting to the chemical contamination and degradation of the PVA matrix [18]. This was different from the results of tensile test, because the modulus of composites was tested by applying tension on the entire sample, thus the interaction between the fibre and the matrix was focused, while the hardness was determined by exerting compression forces on the surface of the composites, thus the hardness of the polymer matrix solely was emphasized.

The hardness of treated composites increased with filler percentage, but decreased in 20% composites. Again, the presence of pores and voids in the matrix of the particular composites sample reduced its ability to withstand the compression force [16].

Thermogravimetric Analysis (TGA)

Figure-6(a) illustrates that the weight percentage decreased with the increment of sample temperature of the untreated composites. The mass reduction could be categorized into 3 stages. The first stage (25–100 °C) was due to the removal of moisture and impurities in the composites. The second stage (300–500 °C) indicated the degradation of PVA matrix, whereas the third stage (500–800 °C) was the result of the degradation of fibre [14].

Figure-6(b) displays the effect of the sample temperature on the reduction of mass percentage of the treated composites from various filler content. Theoretically, the rough surface of alkali treated fibre was expected to induce crystal formation and increase the degree of crystallization in the polymer composites. Therefore, higher temperature should be required to degrade the composites of higher crystallinity. Nevertheless, it was found that the degradation temperature of treated composites (5% and 20%) was lower than that of pure PVA, due to the alkali contamination which resulted in the degradation of the thermal resistance of the materials. The porous matrix in 20% treated composites caused it to have the lowest degradation temperature among all.

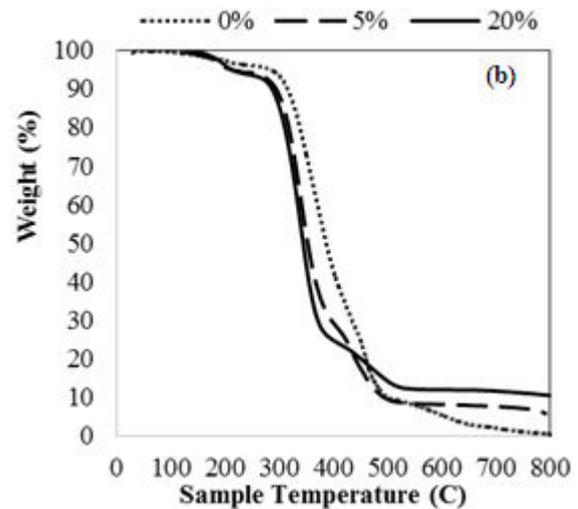
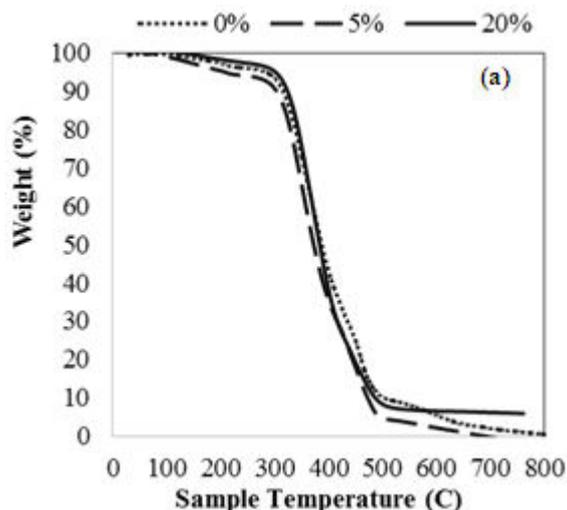


Figure-6. Weight percentage vs. sample temperature of (a) untreated and (b) treated composites film.

There were 5%–10% of residues left upon the end of combustion in 20% untreated composites and in all of the treated composites. This was caused by the incomplete degradation (oxidation) of the sample, due to the improper control of the oxygen flow [14].

Table-3. Degradation temperature of composites from different filler content.

Sample	Degradation temperature (°C)
eat PVA	309
untreated	290
20% untreated	321
5% treated	289
20% treated	285

Table-3 summarizes the degradation temperature of composites from different filler percentage. In comparison, the degradation temperature of 20% untreated composites was the highest. As mentioned, the increased amount of fibre enhanced the interaction between the fibre and the matrix, thus improving its thermal resistance. On the other hand, it was observed that the degradation temperature of 5% untreated composites was lower than the pure PVA. The presence of voids and pores and having the least number of enhancing fibre in the composites were the reason of this phenomenon, in accordance with the SEM results.



Moisture Absorption-desorption Test

Figure-7(a) and 7(b) show the results generated in the moisture absorption test of both untreated and treated composites, where the weight percentage increased with the absorption time. The increment of the mass percentage was attributed to the moisture diffusion into the composites, in three different mechanisms. Firstly, it involves the water molecules diffusion inside the gaps between polymer chains. Secondly, it involves capillary transport into the gaps and flaws at the fibre-matrix interface, due to impaired composites fabrication process. The third mechanism involves the transport of micro-cracks in the matrix, resulted from the swelling of fibres [1].

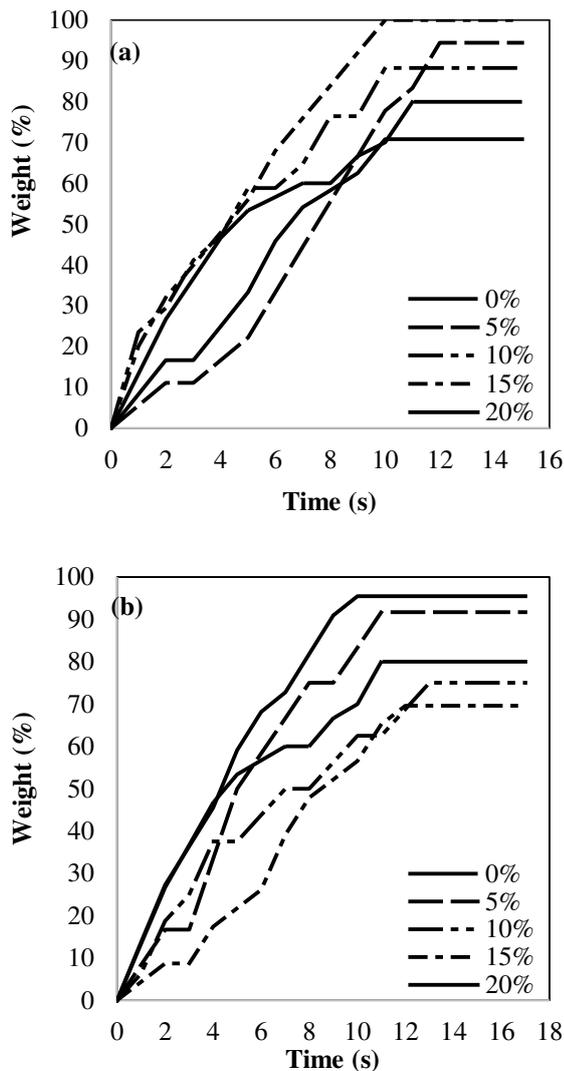


Figure-7. Absorption weight vs. time of (a) untreated and (b) treated composites film.

It was detected that, the moisture absorption ability of both untreated and treated composites deteriorated when the filler percentage increased. This

may be attributed to the decrease of hydrophilicity of the composites with increasing filler content [11]. However, data showed that the 15% untreated composites and 20% treated composites achieved the highest weight percentage for absorbing the greatest amount of moisture. It could be interpreted that this phenomenon was caused by the second and third mechanism of moisture diffusion as mentioned, where the moisture was absorbed into the voids at the fibre-matrix interface, and also into the micro-cracks of the matrix arising from the swelling of fibre after absorbing water.

Figure-8(a) and 8(b) illustrate the decrease in the mass percentage of both untreated and treated composites with the increase of desorption time. It was found that the desorption ability of untreated and treated composites reduced with the increment of filler percentage. Therefore, it could be concluded that, the moisture sensitivity of the untreated and treated composites could be decreased by increasing the amount of fibre.

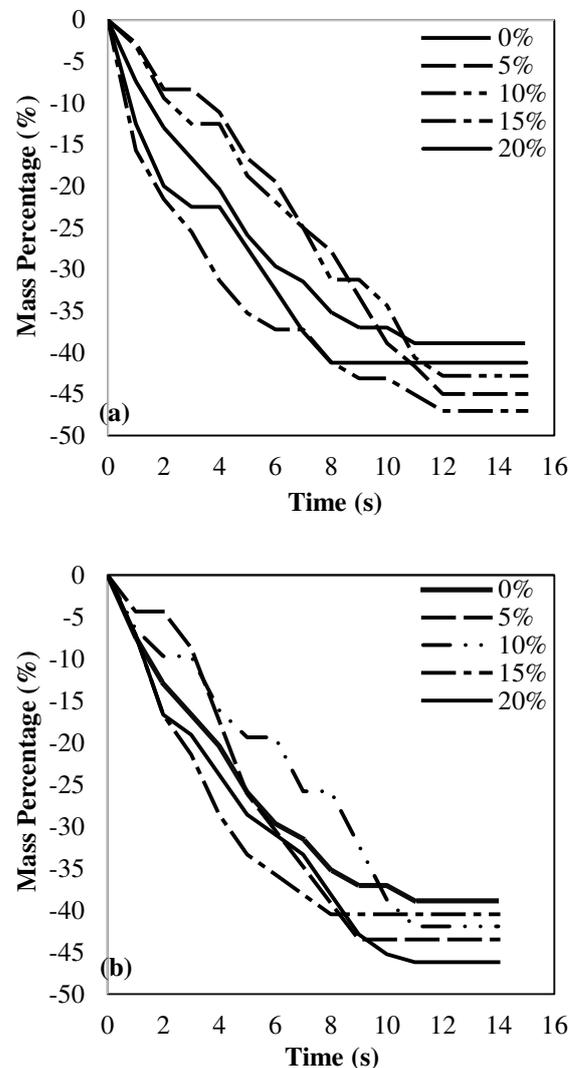


Figure-8. Desorption weight vs. time of (a) untreated and (b) treated composites film.



Nonetheless, it was discovered that the 15% untreated composites and 20% treated composites released the greatest amount of moisture and achieved the lowest mass percentage among all. This was due to the presence of voids and micro-cracks in the components of the composites as mentioned above, which conduced to the ease of moisture desorption.

The average of maximum mass percentage, \bar{M} achieved by the composites from 4 filler compositions was calculated. In moisture absorption test, the value of \bar{M} was 82.9% for treated composites and 88.4% for untreated composites. In moisture desorption test, the treated composites and the untreated composites had \bar{M} of -43.0% and -44.0% respectively. The statistics verified that the alkali modified fibre had greater effect on reducing the moisture absorption and desorption ability of the composites. This was due to the presence of hydrophobic moieties on the fibre surface which increased the moisture resistance of the composites [11]. The moisture content causes degradation in the fibre-matrix interface, which leads to low stress transfer efficiencies, thus resulting in poor mechanical and dimensional properties [1]. Therefore, by increasing the amount of treated fibre, the water resistance of the composites could be improved, thus the degradation of the material could be prevented.

CONCLUSIONS

In the study of the biodegradable fibre-reinforced polymer composites, PVA was successfully integrated with the NaOH modified coconut fibre to form treated composites, and the characterization was carried out to compare with the untreated composites. The results of mechanical properties testing showed that the Young's modulus and the hardness of composites were improved with the increment of fibre volume fraction. The modified fibre had the greatest enhancement on the mechanical properties of composites compared to the untreated fibre, except the properties of a number of treated composites which were degraded due to the alkali contamination. TGA results proved that the addition of fibre would improve the degradation temperature of the composites. Moisture absorption and desorption test verified that the moisture uptake and release ability of composites could be reduced by increasing the treated fibre content. Besides, the treated fibre could further decrease the moisture sensitivity of the composites, compared to the untreated fibre. Conclusively, high content of alkali modified fibre is essential in composites fabrication in order to produce composites with high modulus, high hardness, high degradation temperature, and low moisture sensitivity. The composites material that possesses these properties can be used in the biodegradable food packaging applications and the automotive industries that manufacture vehicle components such as door panels, seatbacks, headliners, and dashboards.

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