IOP Conf. Series: Materials Science and Engineering **368** (2018) 012047 doi:10.1088/1757-899X/368/1/012047

Physical properties of silane-treated sugar palm fiber reinforced thermoplastic polyurethane composites

A Atiqah[1], M Jawaid[1]*, S M Sapuan[2] & M R Ishak[3]

[1]Laboratory of Biocomposite Technology, Institute of Tropical Forestry and Forest Products (INTROP), Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia. [2]Department of Mechanical and Manufacturing Engineering, Faculty of Engineering, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia.
[3]Department of Aerospace Engineering, Faculty of Engineering, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia.

*Corresponding author: jawaid_md@yahoo.co.in

Abstract. Fiber modifications are widely utilized to enhance the interface of fiber and matrix adhesion based on eco-friendly fibers such as sugar palm fibers. The sugar palm (SP) fibers in particle size of 150-250µm were immersed in 2 wt. % silane for 3hrs in this research. Composites of untreated and treated sugar palm fibers reinforced thermoplastic polyurethane (TPU) with different fiber loadings, ranging from 0 to 50 wt. % were then prepared by melt mixing compounding followed by hot pressing moulding. The physical property such as density, water absorption and thickness swelling of the composites were evaluated. Ten replicates of SP/TPU composites with the standard dimension were immersed in distilled water for 168hrs. The chemical changes for untreated and treated through Fourier-transform infrared spectroscopy (FTIR) was done to distinguish the untreated and silane treated of the SP/TPU composites. Increasing the fiber content resulted in higher water uptake and thickness swelling. Moreover, the silane treated SP/TPU composites was shown reducing water absorption and thickness swelling properties. This study is a part of exploration potential application of the composites for automotive part applications.

1. Introduction

Natural fibers are taken from natural plants such as sugar palm, kenaf, flax, and bast which are extracted from its plants, stems, leaves or any part thereof which are classified as an eco-friendly material due its biodegradability and abundance. Sugar palm is one of the best examples that exhibited noteworthy potential to be used as reinforcement in polymer for the development of composite materials [1-2]. On the potential notes, sugar palm has an acceptable standard of strength in its mechanical properties as well as low density, good tolerance in its mechanical and thermal properties [3]. However, on the drawback notes, sugar palm has poor adhesion with polymer matrix. This drawback has extended to be investigated further on the distribution load in reinforcement fibers in order to obtain its maximum strength. Many researchers have tackled this drawback issue by using a certain method such as chemical treatment onto fibers in order to enhance its adhesion to get ideal bonding strength.

The reinforcement between fiber and matrix plays the main role in transferring the stresses performing on the matrix to the fibers. In order to have a good properties of the composites, the fiber

and matrix interface must be strongly attached. Nevertheless, if the interface is too durable, the composite will have the brittle and low stiffness properties. There are numerous reported works to enhance the interfacial bonding between the polymer matrix and natural fibers through fiber treatment modification such as sisal/PLA [4], ijuk/polypropylene [5], pineapple/kenaf/phenolic [6].

One of the common methods to modify the fiber surface properties is by silane treatment. Silane treatment has been discovered to modify the glass fiber surface to be reinforced in polymer matrices. Currently, researches employed the same technique to natural fibers in order to improve the adhesion bonding of fiber/matrix. The fiber treatment enhances the adhesion between the polymer matrix and the surface of fiber by changing the polarity of the fiber surface [7-8].

The previous study conducted by Atiqah, Jawaid, Ishak and Sapuan [9] have investigated the bonding strength of sugar palm reinforced thermoplastic polyurethane. Various treatment such as alkaline, silane and combined alkaline-silane were selected to undergo single fiber test and found that silane treatment showed a good compatible for sugar palm fiber. Silane treatment was employed in modifying natural fiber-polymer matrix interface and improving the interfacial strength. The hydrophobic chemical derivatives of SiH_4 called silane can be hydrolysed and bonded to the hydroxyl groups of cellulose chains [10]. It had been reported that, the cross-linked network between silane treated fibers and the matrix showed non-swelling behaviour and chemical resistance [11].

This paper reports a study of the influence of fiber treatment (silane) on the physical and structure of sugar palm fiber. In order to analyse the physical property of SP/TPU composites, the variation of fiber loading consisted of 0, 10, 20, 30, 40 and 50 wt. % and 2 wt. % of silane treatment were selected in this investigation.

2. Experimental

2.1. Materials

Estane® 58311 TPU was supplied in pellet form with the density of 1.13 g/cm^3 by Pultrusion Sdn. Bhd. and was used as the polymer matrix. The sugar palm fiber (SPF) was collected from sugar palm tree at Jempol, Negeri Sembilan, Malaysia.

2.2. Preparation of Sugar Palm

Firstly, sugar palm fiber was first washed with tap water for several times to get rid of any impurities and dirt that attached to the SPF. The SPF was kept in an open air for 24hrs and dried in an air circulating oven at 60°C for 48hrs. The dry SPF grounded to get the size of 10mm-15mm using plastic crusher machine then followed by using pulverize machine. Next, the particle SPF were sieved to obtain 125-250 μm.

2.3. Silane Treatment of Sugar Palm

The SPFs in particulate size of 125-250 μm were immersed in 2 wt. % of silane for 3hrs. For silane treatment, 3-aminopropyl-triethoxysilane was used and dissolved in a mixture of methanol-water (90/10 w/w) for their hydrolysis. The pH of the solution was adjusted to 3.5 with acetic acid and stirred continuously for 10 minutes. Then, the fibers were immersed in the solution and left for 3hrs under agitation. The SPF were thoroughly rinsed with distilled water and then oven-dried at 60 °C for 72hrs to completely eliminate any moisture effect from the fibers.

2.4. Fabrication of SP reinforced TPU composites

The SP/TPU composites were prepared using melt compounding technique followed by hot moulding process. Sugar palm with particles size of 125-250 μm and thermoplastic polyurethanes in pellet form were dried in an electric oven at 80°C for 48hrs. Six set of neat TPU and SP/TPU composites (0, 10, 20, 30, 40 and 50) wt. % were fabricated. SP/TPU composites were prepared using melt-mixing compounding, followed by hot pressing moulding process to achieve uniform distribution. Haake polydrive R600 was used in the mixing process at the optimum processing parameters temperature,

time and rotating speed; 190 °C, 11 minutes and 40 rpm, respectively. Vechno Vation 40 ton compression molding machine was used in the hot pressing moulding. The samples were pre-heated for 7 minutes at 190°C. Then they were fully pressed for another 10 minutes at 190 °C. Finally, the sample were cold-pressed for 5 minutes at 25 °C. Table 1 shows the composition of the formulation of untreated and treated sugar palm fiber reinforced thermoplastic polyurethane.

Table 1. Designation and composition of the materials.

Materials	TPU (wt %)	SP (wt %)
Neat TPU	100	0
TPU + Sugar Palm Fiber	90	10
TPU + Sugar Palm Fiber	80	20
TPU + Sugar Palm Fiber	70	30
TPU + Sugar Palm Fiber	60	40
TPU + Sugar Palm Fiber	50	50

3. Characterizations

3.1. Physical Properties Testing

Density was measured in air using a digital weighing scale and in water using densimeter, MD-200S Mirage. The difference in weight of the sample in two media gives the weight in gram was converted to volume in $cm^{3.}$

Water absorption specimens of the untreated and treated SP/TPU composites were immersed in distilled water in accordance with ASTM D 570. The SP/TPU composites samples were cut into the size of 20 mm long, 20 mm wide and 3 mm thickness. All specimens were conditioned in and oven at 60° C for 24hrs then put into the sealed plastic bag and cooled in desiccator over granulated silica gel. The samples were then weighed and immersed in a distilled water at room temperature for 72, 150 and 168hrs. Then the specimen was removed from the water, wiped with tissue paper, weighed to measure the weight gain, and put back in the water for continued soaking.

Ten specimens of 20 x 20 x 3 mm samples of each different type of composites were prepared according to ASTM D570 for the testing of thickness swelling.

3.2. FTIR

Fourier transform infrared (FTIR) spectra of the neat TPU, untreated SP/TPU and silane treated SP/TPU composites were tested by using a FTIR machine (SHIMADZU81001. Japan) to evaluate the changes in functional groups on the composites. All spectra were recorded in the range from 4000 cm^{-1} to 350 cm^{-1}.

4. Result and Discussion

4.1. Physical Properties

4.1.1. Density Properties. The results of density measurement of neat TPU, untreated and silane treated SP/TPU composites subjected to different fiber loading were presented as in Figure 1. The density of SP/TPU composites decreased when the sugar palm fibers were treated with silane treatments. It can be seen that neat TPU has lower density (1.07 g/cm^3) neat TPU and SP/TPU composites (10, 20, 30, 40, 50 wt. %) are 1.07, 1.08, 1.14, 1.16 and 1.20 g/cm^3 , whereas the values of density seems to reduce after reinforcing for silane treated fibers which are 1.07, 1.07, 1.09, 1.13 and 1.17 g/cm^3. On the contrary, the density should be higher after fiber treatment, it was suggested that

due to treatment employed on the fiber surface, the fiber cell wall become more compact that increased the density of the fiber [12, 13].

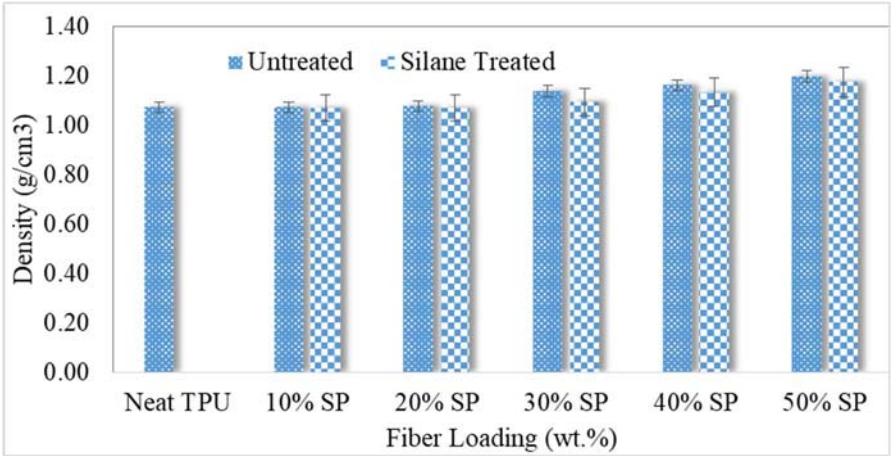

Figure 1. Density of untreated and silane treated SP/TPU composites.

4.1.2. Moisture Absorption Properties. Figure 2 shows the values of the water absorption for the untreated and silane treated of SP/TPU composites, which vary depending upon the fiber loading. As shown in Figure 2, the water absorption of the composites increased with increasing fiber loading, but was lower for neat TPU composites due to the matrix is hydrophobic, whereas the sugar palm fiber composites are hydrophilic. The 2 wt. % of silane treated of SP/TPU composites are significantly lower than those of composites as shown in Figure 2. The gradient of the water absorption graphs for the neat TPU and SP/TPU composites (10, 20, 30, 40, 50 wt. %) are 1.17, 4.23, 4.44, 6.24, 7.47, and 8.21 whereas the values of water absorption for silane treated are 3.24, 3.82, 4.74, 5.73 and 6.83. The neat TPU and 10 wt. % of treated SP composites exhibited less water absorption than those containing 50 wt. % untreated and treated composites. The silane treatment was prone to effective in enhancing the fiber-matrix interface properties [14, 15]. The surface modification of silane after hydrolysis undergo bond formation stage and condensation that induced polysiloxane structures form the reaction hydroxyl groups on the fiber. Hence, the reduction of water absorption of treated SP/TPU composites is due to the improved interfacial adhesion between the TPU chains and the lignocellulosic fiber.

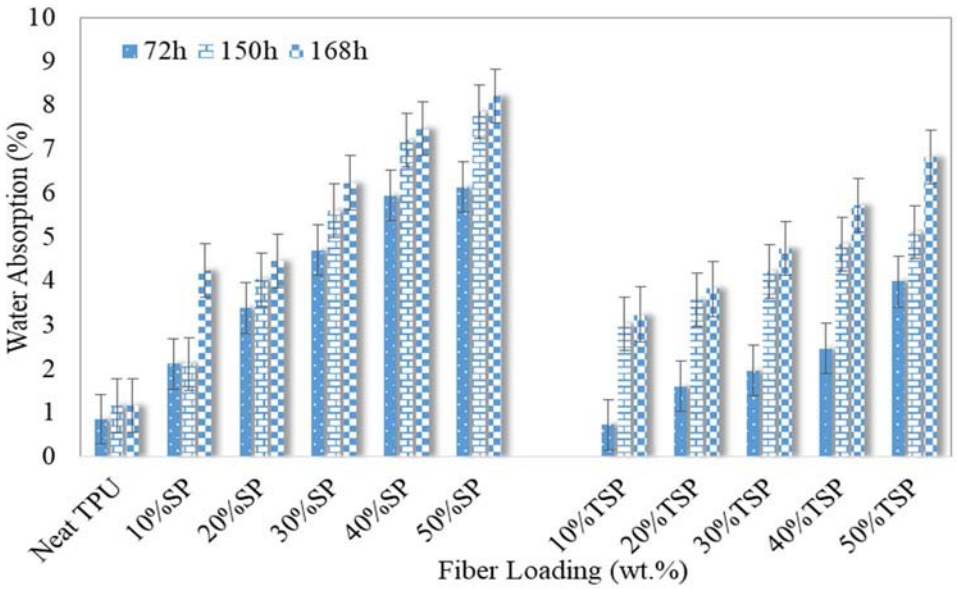

Figure 2. Water Absorption of untreated and silane treated SP/TPU composites.

4.1.3. Thickness Swelling Test . As shown in Figure 3, the thickness swelling of neat TPU, untreated and silane treated of SP/TPU composites were varied according to fiber loading (10, 20, 30, 40 and 50 wt. %). The silane treated of thickness welling are lower as compared than untreated of SP/TPU composites. The gradient of the thickness swelling graphs for the neat TPU and SP/TPU composites (10, 20, 30, 40, 50 wt. %) are 0.99, 3.95, 4.64, 6.18, 7.14 and 7.62 whereas the values of water absorption for silane treated are 3.11, 5.49, 6.28, 5.62, and 6.84. In this case, the higher loading of sugar palm fiber exhibited the higher thickness swelling. However, the treated fiber loading of 40 wt. % showed the less thickness swelling as compared to other formulations. According to Agrawal, Saxena, Sharma, Thomas and Sreekala [16], silane treatments may reduce the number of cellulose hydroxyl group in the surface of the fiber and polymer matrix. The silanols group were formed due to the presence of the hydrolyzable alkolyl group from the moisture that existed on the fiber surface. Then, the silanols react with the hydroxyl group of the fiber to form the stable covalent bonds to the outer cell wall so that the chemical easily absorbed onto the fiber surface. Thus, the hydrocarbon chain that induced by the employing of silane treatment detains the swelling of the fiber by creating a cross-linked network because of covalent bonding between the fiber and matrix.

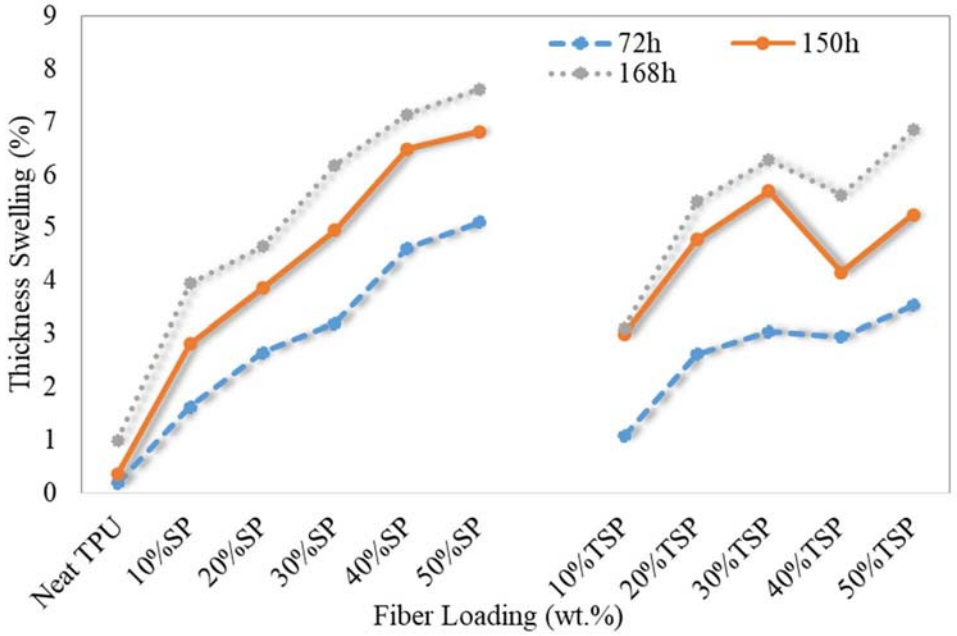

Figure 3. Thickness swelling of untreated and silane treated SP/TPU composites.

4.2. Chemical and Morphological Analysis

4.2.1. FTIR. Figure 4 exhibits the FTIR spectra of the neat TPU, untreated and silane treated sugar palm fibers reinforced TPU (SP/TPU) composites. To attain good physical properties of the composites requires a good interface between fiber and matrix. The sugar palm fiber was treated with silane treatment to improve the interfacial adhesion between sugar palm fibers and TPU matrix in this study. Figure 4 shows the untreated SP, which showed similar attributions nearly the neat TPU. The chemical structure of absorption peak at 921 cm^{-1} was due to the Si-O vibration [17], which agreed on the confirmation of 3-aminoporpyltriethoxysilane of treated SP/TPU composites. The presence on chemical structure as observed in Figure 4 conformed that the silane chemical structure are existed on the sugar palm fibers. The possible chemical structure that existed on the neat TPU, untreated and silane treated were tabulated in Table 1.

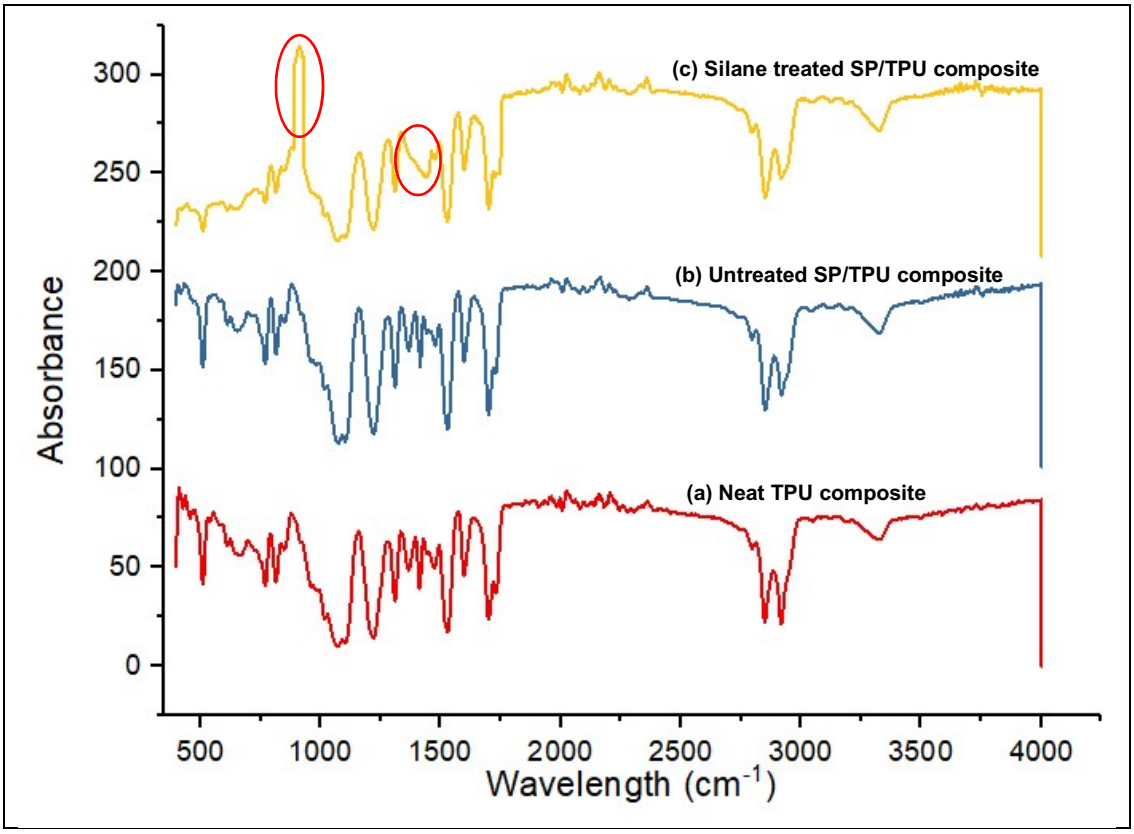

Figure 4. Spectrography from FTIR on neat TPU and untreated fibers (a) neat TPU, (b) untreated SP/TPU composites and (c) silane treated SP/TPU composites.

Table 2. The wave numbers of peaks used for FTIR analysis and corresponding functional groups and vibrational type of neat TPU, untreated and silane treated SP/TPU composites [18-19].

Peak Location (cm^{-1})	Chemical Structure	Motion	Neat TPU	Untreated SP/TPU composites	Silane Treated SP/TPU composites
1510-1550	H-N-CO	Combined motion	1531.228	1535.085	1531.228
1690	C=O	Associated urethane	1700.936	1700.936	1700.936
1740	C=O	Non-bonded urethane Stretching	1731.792	1729.863	1727.935
2800-3000	CH_2 and CH_3	Stretching	2917.818	2919.747	2919.747
1590-1650	N-H	Bending	1627.653	1598.728	1629.851
3200-3420	N-H	Stretching	3330.517	3328.588	3332.445

5. Conclusion

In this study, the SP/TPU were successfully prepared with fiber treatment of silane. The experimental results showed that the physical of TPU based were improved with the incorporation of 50 wt. % of SP and 2 wt. % silane treatment of fibers. The silane treated of SP/TPU reduce the density, water

absorption, and thickness swelling properties was the minimum for 40 wt. % of SP compared with those of untreated sugar palm fiber which enhances their suitability for automotive components.

Acknowledgment
The authors are grateful for the financial support from Universiti Putra Malaysia through Putra grant no. GP-IPS/2015/9441501. The author would also like to thank the Ministry of Higher Education for the MyBrain15 scholarship.

References

[1] Mogea J, Seibert B and Smits W 1991 Multipurpose palms: the sugar palm (Arenga pinnata (Wurmb) Merr.) *Agroforestry Systems* **13** 111-29
[2] Sanyang M L, Sapuan S, Jawaid M, Ishak M R and Sahari J 2016 Recent developments in sugar palm (Arenga pinnata) based biocomposites and their potential industrial applications: A review *Renewable and Sustainable Energy Reviews* **54** 533-49
[3] Ishak M, Sapuan S, Leman Z, Rahman M, Anwar U and Siregar J 2013 Sugar palm (Arenga pinnata): Its fibres, polymers and composites *Carbohydrate polymers* **91** 699-710
[4] Orue A, Jauregi A, Unsuain U, Labidi J, Eceiza A and Arbelaiz A 2016 The effect of alkaline and silane treatments on mechanical properties and breakage of sisal fibers and poly(lactic acid)/sisal fiber composites *Composites Part A: Applied Science and Manufacturing* **84** 186-95
[5] Zahari W, Badri R, Ardyananta H, Kurniawan D and Nor F 2015 Mechanical properties and water absorption behavior of polypropylene/ijuk fiber composite by using silane treatment *Procedia Manufacturing* **2** 573-8
[6] Asim M, Jawaid M, Abdan K and Ishak M R 2016 Effect of Alkali and Silane Treatments on Mechanical and Fibre-matrix Bond Strength of Kenaf and Pineapple Leaf Fibres *Journal of Bionic Engineering* **13** 426-35
[7] Kushwaha P K and Kumar R 2010 Studies on water absorption of bamboo-epoxy composites: Effect of silane treatment of mercerized bamboo *Journal of applied polymer science* **115** 1846-52
[8] Goriparthi B K, Suman K and Rao N M 2012 Effect of fiber surface treatments on mechanical and abrasive wear performance of polylactide/jute composites *Composites Part A: Applied Science and Manufacturing* **43** 1800-8
[9] Atiqah A, Jawaid M, Ishak M R and Sapuan S M 2017 Effect of Alkali and Silane Treatments on Mechanical and Interfacial Bonding Strength of Sugar Palm Fibers with Thermoplastic Polyurethane *Journal of Natural Fibers* 1-11
[10] Saha P, Chowdhury S, Roy D, Adhikari B, Kim J K and Thomas S 2016 A brief review on the chemical modifications of lignocellulosic fibers for durable engineering composites *Polymer Bulletin* **73** 587-620
[11] Thakur M K, Gupta R K and Thakur V K 2014 Surface modification of cellulose using silane coupling agent *Carbohydrate polymers* **111** 849-55
[12] Ticoalu A, Aravinthan T and Cardona F 2014 A study into the characteristics of gomuti (Arenga pinnata) fibre for usage as natural fibre composites *Journal of Reinforced Plastics and Composites* **33** 179-92
[13] Sawpan M A 2010 Mechanical performance of industrial hemp fibre reinforced polylactide and unsaturated polyester composites. The University of Waikato)

[14] Abdelmouleh M, Boufi S, Belgacem M N and Dufresne A 2007 Short natural-fibre reinforced polyethylene and natural rubber composites: effect of silane coupling agents and fibres loading *Composites science and technology* **67** 1627-39
[15] Zhou F, Cheng G and Jiang B 2014 Effect of silane treatment on microstructure of sisal fibers *Applied Surface Science* **292** 806-12
[16] Agrawal R, Saxena N, Sharma K, Thomas S and Sreekala M 2000 Activation energy and crystallization kinetics of untreated and treated oil palm fibre reinforced phenol formaldehyde composites *Materials Science and Engineering: A* **277** 77-82
[17] Satyanarayana N, Xie X and Rambabu B 2000 Sol–gel synthesis and characterization of the Ag 2 O–SiO 2 system *Materials Science and Engineering: B* **72** 7-12
[18] Aji I, Sapuan S, Zainudin E and Abdan K 2009 Kenaf fibres as reinforcement for polymeric composites: a review *International Journal of Mechanical and Materials Engineering* **4** 239-48
[19] Kabir M, Wang H, Lau K and Cardona F 2012 Chemical treatments on plant-based natural fibre reinforced polymer composites: An overview *Composites Part B: Engineering* **43** 2883-92