Sodium Hydroxide/Silane Treated Kenaf Fibre in Unsaturated Polyester Matrix: Effects of Fibres Length and Fibres Loading Towards The Composites Flexural and Morphological Properties

Muhammad Mustakim Mohd Ghaztar
Faculty of Applied Sciences, Universiti Teknologi MARA,
40450 Shah Alam, Selangor, Malaysia.

*Nik Noor Idayu Nik Ibrahim**
Centre for Chemical Synthesis and Polymer Technology, Institute of Science,
Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia.
**nikidayu@uitm.edu.my*

Ahmad Zafir Romli
Faculty of Applied Sciences, Universiti Teknologi MARA,
40450 Shah Alam, Selangor, Malaysia.

ABSTRACT

The fibre behaviour is a critical aspect that will determine the deformation of the composite since it highly relies on its physical and chemical properties. This paper focus on the effect of similar fibres aspect ratio (L/D) with different length of untreated Kenaf fibre and Sodium Hydroxide/silane treated Kenaf fibres on the flexural properties of the composites. The treated and untreated kenaf fibre at two different fibre lengths (A: 0.4 cm and B: 2.9 cm) were fabricated at low filler loadings (5,10,15%) and high filler loadings (45,50,55%). The results showed an improvement in the flexural stress (7-44 %) and modulus (6-46 %) with the application of treatments for both A- and B- fibre categories. The optimum result was achieved from the treated samples at a shorter A-fibre composite, although the aspect ratio between A and B-fibre samples are similar. The chemical treatment coalition might improve the

ISSN 1823-5514, eISSN 2550-164X
Received for review: 2021-07-13
Accepted for publication: 2021-12-13
Published: 2022-04-15

surface interaction and, at shorter fibre length, it affects the fibres compactability that led to an improvement in stress distribution and low voids formation as supported by the observation on the composite's fractured surface where traces of matrix observed on the surface of pull-out fibres. From the fractographic analysis, the fibres morphological condition before the fabrication is one of the important factors to consider since it can affect the end-properties of the composites.

Keywords: *Kenaf Natural Fibres; Sodium Hydroxide; Silane Treatments; Fibres Aspect Ratio; Flexural Properties*

Introduction

Further research that relates to fibre behaviour during the application of force is required to optimise the properties and capability of the composite system, considering that the way of the fibre response when received the load applied at low or high intensity; and at any part of fibre will determine the reinforcing mechanism of the fabricated fibre in a composite system. The fibre reinforced composite produced is expected to inherit both properties of fibre and matrix and displaying new properties as it usually becomes stiffer than matrix. Typically, synthetic-based fibre will be fabricated for load loading applications but, due to the cost aspect (tool maintenance, selling) and environmental impact (soil fertility), the trend of fibre reinforced applications is shifted to a greener material [1-5].

The green materials are usually extracted from animal and plant-based materials and are known as renewable resources [6-8]. Plant-based materials, despite their merits, possessed some drawbacks especially the inconsistency in materials length, diameter and aspect ratio as highlighted by Ghaztar and Romli [9]. For plant-based material, it is well-known for its natural inconsistency that is influence by the maturity of the plants, sunlight exposure, minerals and water permeation as well as the parts of the plant taken since it differed between its bottom and tip. All these plant growth sources will affect the size of the extracted parts especially at the fibrous bast part of the plant [10]. The inconsistency of plant-based material further narrows to its mechanical aspect. Since there are many types of natural fibres and they also have various structure [11] at its inner and outer parts of the fibre (e.g. the size of the lumen and fibrils). Therefore, the fibres ability to absorb the load, retain in its structure as well as disperse well throughout the region of the composite are different. The structure of the fibres also changed after passing thru the material fabrication machine. For instance, the usage of mechanical size reduction technique to shorten the fibre size, since the fibre is repeatedly cut before passing thru the mesh aperture and worsen when using the smallest mesh size. The size reduction process also will directly influence the aspect

ratio of the fibre, which is one of the important factors in determining the performance of the composites. Aspect ratio, which is defined as the ratio of fibre length to the fibre diameter, in general, will increase the composites' strength as the aspect ratio increases. High aspect ratio reinforcement capable of providing higher contact area for adhesion which will significantly change the composites' physical and mechanical properties.

In the morphological aspect, the irregular shape fibre might influence the composites behaviour in crack initiation, propagation and composites debonding. Since the fibres shape inconsistency might react differently than the expected properties even for samples in the same batch and vigilant control in processing and fabrication technique. For chemical aspect, the difference in chemical constituent, polarity (hydrophilic), crystalline region, fibrils direction [12, 13] and surface interaction influence to the inconsistency in natural fibre. These factors might influence the fibres ability to strengthen the fibre structure to retain the load applied especially in mechanical properties. Currently, the trend that practice by the natural-based fabricator is by optimising the interaction on the surface of the fibre. It can be implemented using chemical, plasma, nanocellulose coating, enzymes and fungi treatment methods [14-16]. But, by considering the cost and practicality aspects, the chemical treatment is better since it is well-practised by industrial players. Namely, the mercerisation, acetylation, peroxide, permanganate, isocyanate, polymer grafting, silanisation and benzoylation [14].

Recently, the trend of combining of these chemical treatments (coalition) have getting more attention since this method has the capability of providing a synergistic effects in enhancing the properties of the composites [17-21]. According to [17, 22, 23], the treatment of the natural fibre with the Sodium Hydroxide (NaOH) followed by the Silane treatment (three-aminopropyltriethoxysilane) had significantly improve the tensile, flexural and impact properties due to better adhesion between the fibre and the matrix. The storage modulus of NaOH-Silane treated kenaf fibre had increased 87% compared to the NaOH-treated and Silane-treated alone where the reinforcement imparted by the fibres at 25 °C had 161% of modulus increment whereas the other treatment is not even reach 100% increment. NaOH-Silane treated fibre also exhibited better stability at higher temperature whereas at 60 °C, NaOH-Silane treated composites showed the highest value of storage modulus compared to the others. In another study by Orue et al. [23], hardly pull-out fibre can be observed on the facture surface when examined under the Scanning Electron Microscope (SEM). In addition, it is difficult to distinguish the fibres from the matrix which indicating a good coating formed between the fibre and the matrix as a result of the NaOH-Silane treatment. Despite of all that, the effect of NaOH-Silane treatment on the thermoset system is still in question whereby only few literatures had been discussing on the matter. All of the literatures mentioned had been using thermoplastic as a matrix (e.g: PLA [22, 23] and PP [17]). Sreenivasan et al. [24] had studied the effect of the

combined treatment of Kenaf, Abaca and Oil Palm Fibres reinforced unsaturated polyester matrix whereby the effect of treatment time had been compared at a fixed percentage of fibre loading (fibre volume fraction). They found that the ultimate tensile strength of NaOH-Silane treated composites had been in between those of NaOH-treated and Silane-treated which said to be contributed by the partial removal of lignin and other soluble compounds resulted in the incomplete cleaning of the fibre surface. It can be said that the combined-treatment of NaOH and Silane has the potential to improve the fibre-matrix adhesion when factors such as treatment process and procedures, fibre's aspect ratio, and fibre loading are taken into consideration.

In the present study, the coalition effect of chemical treatment on the flexural properties of Kenaf/unsaturated polyester (UP) composites from the aspect of fibre loadings (high and low fibre loadings) and fibre length were discussed since the fibre volume fraction is one of the factors that influence the ability of randomly oriented short fibre to efficiently exhibit stress-transfer in a composites system. In addition, the fibres' aspect ratio also influences the composites' performance since, in general, as the aspect ratio increases, the composites' strength increases. The effect of fibres of similar aspect ratio but with different fibres' length on the composites' flexural properties was also presented.

The Kenaf fibres were subjected to a chemical treatments coalition of mercerise (NaOH) and silanise (aminosilane) in order to modify their surface interaction. NaOH treatment is capable to alter the surface topography of the fibre resulting in mechanical interlocking where it changes the direction of the fibrils to the load loading direction. In addition, the NaOH treatment is able to convert the amorphous region of the fibre into a crystalline structure making the fibre stiffer. The fibres were also subjected to the silane treatment since the treatment is proven capable of creating a strong covalent bonding like a 'chemical bridge' to link fibre and matrix to decrease the effect of the polarity difference in a composite system. Figure 1 shows the reinforcing mechanism of untreated and NaOH/ Sil treated fibres in composites samples. The synergistic effects of these treatments are combined with the usage of peroxide initiator (MEKP) that claimed able to create the more reactive site of covalent bonding which can increase the surface interaction between the fibre and the matrix during the fabrication process.

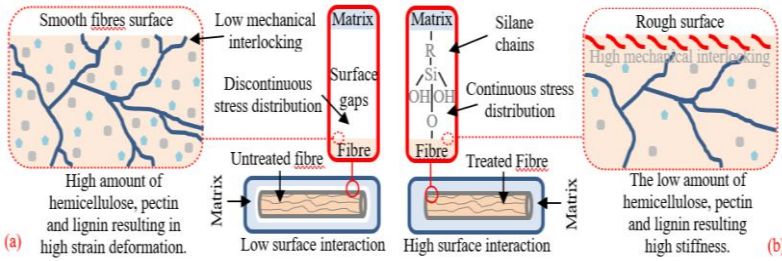


Figure 1: The illustrations of reinforcing mechanism of (a) untreated and (b) NaOH/ Sil treated fibres composites in physical, chemical, and mechanical aspects

Materials

Kenaf fibre was obtained from the National Kenaf and Tobacco Board (NKTB) with a length of around 30 cm. The physical and mechanical properties of Kenaf bast fibres are listed in Table 1. Unsaturated polyester (UP) Reversol (RP) 9509 was manufactured by Revertex (Malaysia) Sdn. Bhd. It contains 41-44% of styrene and 56-59% of polyester with viscosity of 450-6000 cps at 25 ºC and become rigid when harden. The tensile strength and elongation at break is 62 MPa and 2.2%, respectively, with hardness of 40 (Barcol Impressor) [26]. Methyl Ethyl Ketone Peroxide (MEKP) Butanox M-50 containing 30-37% of peroxide with 210.22 g/mol of molar mass and a density of 1.170 g/cm^3 was used as curing initiator.

Table 1: The physical and mechanical properties of Kenaf bast fibres

Fibrous	Material	Kenaf (Bast)
Density (g/cm^3 fibres)	Fibres	-
	Bundle	1.2
Lengths (mm)	Range	1.4-1.1
Diameter (μm)	Average	2.6
	Range	12-36
Length / Diameter	Average	21
	Ratio	124
Tensile	Average and Specific	295-930 & 246-993
	Average and Specific Modulus (GPa)	22-60 & 18-50

Source: Physical and mechanical properties of commercially important lignocellulosic fibre and of E-glass fibre [25].

Methodology

Fibres treatment process

The kenaf fibres were divided into two batches. One batch is left untreated (control), and the other is treated with Sodium Hydroxide (NaOH)/Silane. The treatment was carried out by soaking the fibres with 6% w/v NaOH solution for 3 hours before being washed and dried at 70 °C for four days. The fibres were then treated with 3-aminopropyltriethoxy silane (APS) at 1% v/v concentration in 95% v/v diluted ethanol for 30 minutes prior to air-dried. 6% w/v concentration of NaOH and 3 hours immersion time were chosen based on the literature where sufficient cleaning effect and properties improvements were obtained without inflicting excessive corrosion to the fibre's surface [27-29]. On the other hand, 1% v/v concentration of Silane and 30 minutes immersion time were chosen where optimum properties were obtained in the literature. Higher concentration and longer immersion time reduced elongation at break [30, 31].

Pulverisation of Kenaf fibres

The fibres were cut using Fritsch Power Cutting Mill Pulverisette 15 using 5.0 mm and 0.25 mm pulverise mesh aperture to obtain short and long fibres length, respectively. The fibres were passed three times using the same mesh aperture, and the size of the fibres changed was measured using a polarised optical microscope. Table 2 lists all the formulations and samples coding. 5, 10, and 15 wt% fibre loading were selected for the low filler loading category to study the influences of fibres length in high matrix content conditions. On the other hand, 45, 50, and 55 wt% fibre loading were selected for the high filler loading category to study the influences of fibres length in a situation where the matrix and fibres were in a similar percentage. 55 wt% was selected as the highest fibre loading for this study since higher fibre loading is expected to reduce the properties due to the possibility of matrix starve.

Table 3 shows the range and diameter of Kenaf fibres. Different fibres' diameter was obtained during the pulverization process by passing thru the fibres through a different mesh size filter. In this context, mesh size is defined as a hole's diameter of the filter. 0.25 mm mesh size filter produced shorter and smaller fibres than the 5.0 mm mesh size filter.

Table 2: Kenaf/UP composites formulations and samples coding

Classification	**Compositions (wt %)**		**Samples Code**			
			A – Fibre (Short) (7.54 ± 0.41 Aspect Ratio) (0.39 ± 0.24 mm Length)		**B – Fibre (Long)** (7.5 ± 0.64 Aspect Ratio) (2.9 ± 0.82 mm Length)	
	UP	**Kenaf Fibre**	**Untreated**	**Treated**	**Untreated**	**Treated**
Low Fibre Loading	95	5	5FUnA	5FTrA	5FUnB	5FTrB
	90	10	10FUnA	10FTrA	10FUnB	10FTrB
	85	15	15FUnA	15FTrA	15FUnB	15FTrB
High Fibre Loading	55	45	45FUnA	45FTrA	45FUnB	45FTrB
	50	50	50FUnA	50FTrA	50FUnB	50FTrB
	45	55	55FUnA	55FTrA	55FUnB	55FTrB

Note: The pristine UP matrix is coded as 0F.

Table 3: Range and average diameter of A and B Kenaf fibres

	A – Fibre (Short)	**B – Fibre (Long)**
Mesh Size (mm)	0.25	5.0
Aspect Ratio	7.54 ± 0.41	7.5 ± 0.64
Fibre Length (mm)	0.39 ± 0.24	2.9 ± 0.82
Fibre Diameter:		
Range (mm)	0.079 – 0.021	0.498 – 0.242
Average (mm)	0.052	0.388

Preparation of Kenaf/unsaturated polyester composites

UP and MEKP were weighted and mixed at 100 to 3 ratios. Then, the Kenaf fibres (in short fibre form) were added into the mixture of UP and MEKP and stirred using a mechanical stirrer. The mixture was then poured onto the 150 cm (length) x 150 cm (width) steel mould and subjected to the initial cure using a hot press machine for 40 minutes at 70 °C and post-cured in an oven at 70 °C for 24 hours. The samples of randomly oriented discontinuous fibres were fabricated in two categories of fibre loadings which are low loadings (5, 10, 15 wt%) and high loadings (45, 50 and 55 wt%), and at two fibre's lengths which are short length (A-fibre) of about 0.39 ± 0.24 mm and long length (B-fibre) of about 2.9 ± 0.82 mm.

Testing and characterisation process of Kenaf/unsaturated polyester composites

Flexural test

The test was referred to ASTM D790-10 [32] using Shimadzu Universal Testing machine (AG-20 kNX) at a crosshead speed of 5 mm/min. Minimum of five samples with dimension of 15 cm length x 2 cm width x 0.3 cm thickness were tested with the application of 2N pre-force. The length of support span for each sample was calculated using Equation (2). Figure 2 shows the layout of flexural test.

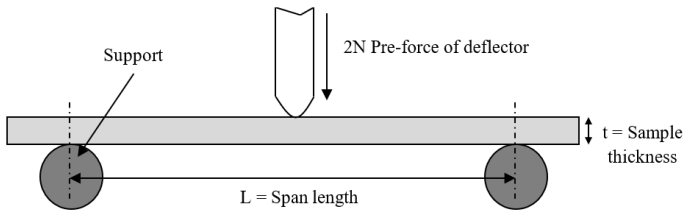


Figure 2: Layout of the flexural test [26]

The samples support span was calculated using Equation (2) that originate from Equation (1). The value of crosshead speed, R and rate of outer fibre straining, Z is constant which are 5 mm/min and 0.01 mm/mm/min respectively.

$$\text{Crosshead speed, } R = (ZL^2)/6d \quad (1)$$

$$\text{Sample support span, } L = (6Rd/Z)^{1/2} \quad (2)$$

where, R (unit: mm/min) is the crosshead speed, Z (mm/mm/min) is the straining rate of the outer fibres, L (unit: mm) is the samples support span and, d (unit: mm) is the sample diameter or thickness. The specific flexural stress and modulus were calculated from Equation (3) and (4) respectively.

$$\text{Specific flexural stress, } \sigma F = (3PL/2bd^2)/\rho \quad (3)$$

where, σF is the flexural stress, P is the load at the given point on the load-deflection curve, L is the length of the support span, b is the width of the sample, d is the depth of tested sample and ρ is the samples density [33].

$$\text{Specific flexural modulus, } E_B = (L^3\, m/(4bd^3)/\rho \quad (4)$$

where, L (mm) is the support span length, m is the tangent slope of the load-deflection curve (N/mm), b (mm) is the width of sample, d (mm) is the depth of sample and ρ is the density of the sample [33].

Samples fractured surface analysis

The morphological analysis was conducted using a polarised optical microscope model Olympus BX51 as referred to ASTM ASTM F1877-98 [34]. The image of individual fibre fractured was captured using the dark field in reflected light at 10x magnification.

Result and Discussions

Flexural properties

Figure 3 shows the specific flexural stress for all samples. The result showed that the flexural stress for all filled samples was lower than the 0F sample. The presence of fibre might be influencing the specific flexural stress since it contributed to the low resistance of bending force. This might be due to the fibre inhibiting the 3-dimensional crosslink of UP matrices in the composite system. Therefore, the filled samples lose the rigidness property to give lower deformation as the vertical force is applied. Even at 5% fibre loading, which supposedly has a higher portion of the strong matrix, the flexural strength has drastically reduced, especially for untreated fibre composites. This might be contributed by the fact that the ability of randomly oriented short fibre to efficiently exhibit stress-transfer depends on the fibre volume fraction and the ratio of E_f/E_m (rule-of-mixtures). In addition, low surface adhesion between the fibre and the vicinity resin had further reduced the flexural strength of the composites since the tendency of the voids to exist in between the fibre-matrix interphases is high.

As the percentage of fibre loading increased from 5% to 15%, the specific flexural stress also increased. This trend was observed for both categories of fibre's length and also for the untreated and treated fibres. However, the treated fibres exhibited higher specific flexural stress than the untreated. The increasing trend for low filler loading composites might be contributed by the higher fraction of matrix resin which produced better fibre wettability and stronger fibre-matrix adhesion. On the other hand, a decreasing trend of specific flexural stress was obtained for the high fibre loading composites when the fibre's loading increased. A low fraction of the matrix restricted the ability of the matrix to thoroughly wet and bind the fibres, which resulted in the inefficient stress transfer mechanism due to the formation of the intratow voids on the surface of the fibres.

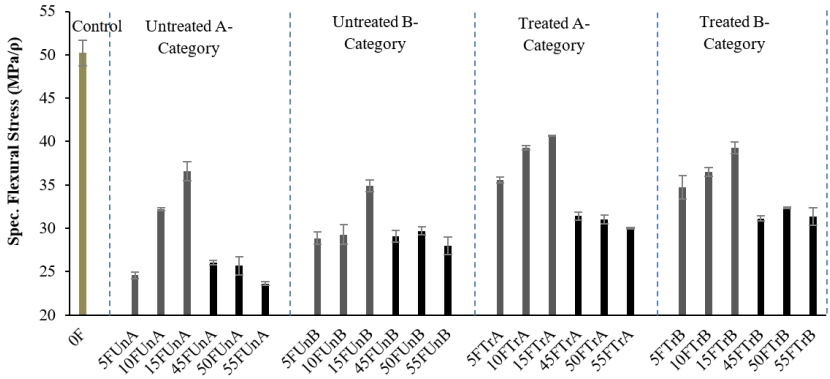


Figure 3: The specific flexural stress for A and B-fibre categories for both treated and untreated samples

When comparing the chemical treatment aspect, the TrA and TrB composites recorded higher specific flexural stress than the UnA and UnB composites. The coalition of chemical treatment seems to have a positive impact on the composite strength. The treatment of the fibres with the NaOH solution had modified the surface of the fibre in a way that the fibre's surface becomes roughen where the matrix resin will fill in the rough surface forming a mechanical interlocking mechanism that will increase the capability of the composites to carry more loads. On the other hand, the silanization of the fibre will improve the fibre's compatibility with the matrix, which is an essential factor for the consistency in the strength of the composites. This finding is also in line with researches made by Ghaztar et al. [35].

From the aspect of fibre's length, even having the same aspect ratio and contact area, the specific flexural stress seems to be affected by the fibre's length. Fibres A, which have a shorter length exhibited higher tensile stress for the low loading category. On the other hand, for high filler loading, Fibre B revealed higher flexural stress. The same trend was also observed for the untreated and treated samples. At low filler loading, where the matrix dominates the composites system, shorter fibre length seems to exhibit better stress distribution which resulted in higher flexural modulus. However, Fibre-B exhibited higher flexural stress at high filler loading than Fibre-A, especially for the untreated samples, which might be due to the effect of bulk fibres which enhanced the resistivity of the composite to the deformation up to the 50% fibre loading before dropped back at 55%. In addition, it can be said that the treated fibres exhibit higher flexural stress for both Fibre A and Fibre B at low and high loading since the fibre-matrix adhesion is better.

For the specific flexural modulus, 0F sample showed the lowest value, as shown in Figure 4. Since the pristine UP system consists of a dense 3-

dimensional network, the applied stress can be efficiently distributed throughout the composite system, which allows the sample to deflect at a higher load, which increases the strain. Less void content due to the absence of fibres also creates a continuity of stress distribution.

Similar to the specific flexural stress, the TrA and TrB samples showed higher in specific flexural modulus compared to the UnA and UnB samples. The coalition of chemical treatments might produce cleaner fibres where the foreign matters and impurities were removed during the NaOH treatment and, when combined with the silane treatment, had resulted in the continuous good interphases adhesion without disruption from the foreign particles. This condition also lowers the possibility of voids formation between the phases, giving a compact composites system where the resistance to the flexural deformation is improved. This is supported by the optical image on the fractured sample where the matrix efficiently binds the fibres, preventing them from being pulled out.

Another factor contributing to the higher flexural modulus of TrA and TrB samples is the increment of crystalline cellulose of fibres. The fibre initially from cellulose I (anti-parallel chain) was converted to cellulose II (helical chain) after being subjected to NaOH treatment. The amorphous region in the fibre was convert ed to the crystalline region, thus increasing the density of the fibre. It also reduces the hemicellulose content making the interfibrillar region less dense and rigid. This imparts to the loose bond structure, which enables the fibrils to be aligned to the stress loading direction and contributes to the increment in modulus property [36].

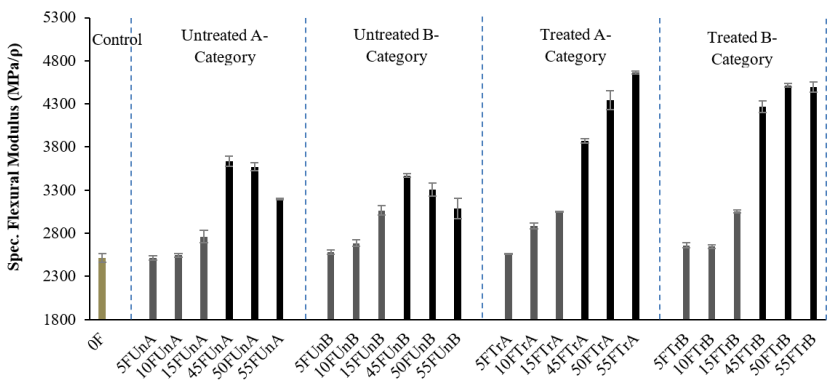
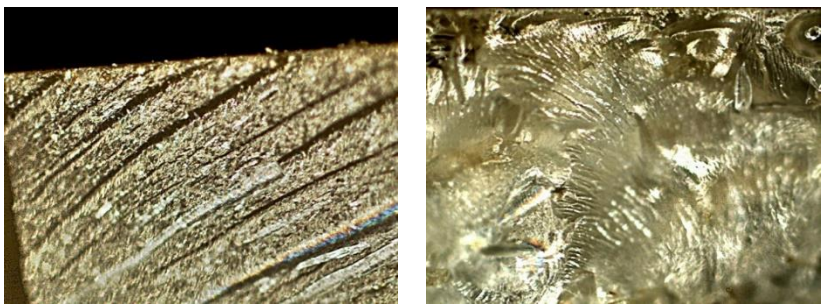


Figure 4: The flexural modulus of A and B-fibre categories for both treated and untreated samples

Morphological analysis

Figure 5 shows the wavy slip streaks of unfilled and filled samples. For pristine UP, the sample fractured in a uniform wavy slip streaks (brittle-like failure) without any formation of crazing correspond to the brittle nature of cured UP. On the other hand, filled samples fractured in inconsistent wavy formation since the presence of the fibres diverge the stress flow in multiple direction.



(a) (b)

Figure 5: The polarised optical fractographs of wavy slips of (a) unfilled and (b) filled fractured samples surface observed under dark field in reflected light at 10x magnification

Figure 6 shows the optical micrographs of (a) low fibre loading and (b) high fibre loading sample taken on the surface of the samples. As can be seen from Figure 6 (a), the low fibre loading sample appeared to be "matrix rich" where all fibres are completely embedded within the matrix.

However, for the high fibre loading sample, there are some region where the fibres are exposed due to the "matrix starving" which resulted in the incomplete fibre wetting, low fibre-fibre interaction and reduction in the composites compactness as can be seen from Figure 6 (b), causing disruption to the stress transferring from the matrix to the fibre. This explained the increasing and decreasing trends of specific flexural strength for the low fibre loading and high fibre loading composites, respectively. Figure 6 (c) and (d) shows the different in fibre-matrix interaction at the interface for the untreated and treated composites, respectively. A gap between the fibre and the vicinity matrix can be seen from the enlarge section in Figure 6 (c) which indicating a low adhesion between the fibres and the matrix since the fibre was not treated. On the other hand, the adhesion of fibres to the vicinity matrix in treated composites seems to be stronger since there is no gap observed.

Figure 7 (a) and (b) shows the debonding of treated fibres taken at the fractured surface. The pulled-out fibres exhibit axial splits and fibrils debonding. In addition, traces of UP matrix observed on the surface of the fibre's pull-out indicating a strong adherence of matrix to the fibre.

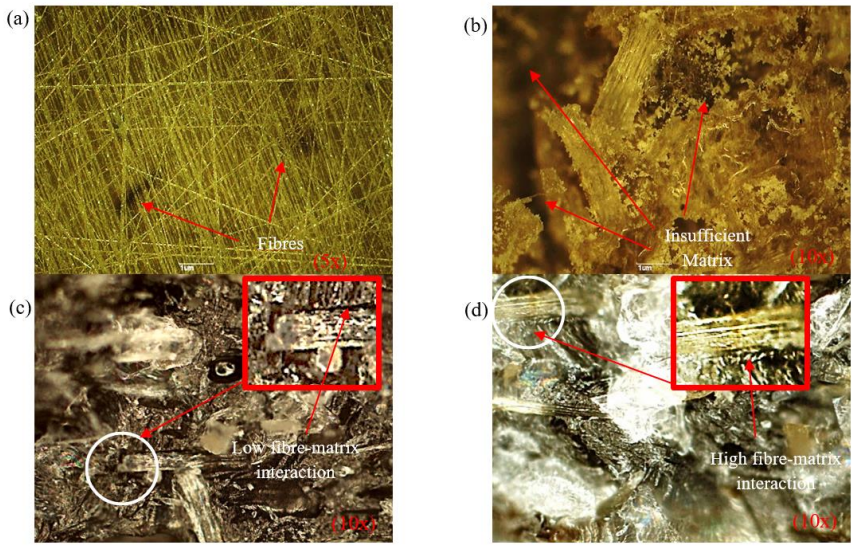


Figure 6: The polarised optical micrographs of (a) 5% and (b) 55% w/w NaOH/Sil fibre loadings. Comparison of low fibre-matrix interaction between surfaces of low and high fibres loading samples. Fibre-matrix surface bonding difference between (c) untreated and (d) treated fibres at low filler loading observed under dark field in reflected light at 5x and 10x magnifications

Figure 7 (c) and (d) shows the difference in stress concentration streaks of treated fibres between short (TrA) and long (TrB) fibres. The TrA fibre appeared to have short length stress concentration compared to the TrB fibre. It might be influenced by the size of the fibre, since smaller fibre's size absorbed small amount of stress before passing the stress to the adjacent fibres. Thus, with the abundant numbers of small TrA fibres, the stress is distributed efficiently and generating small area of stress streaks which is vice versa for TrB fibre.

Optical micrographs in Figure 8 (a) and (b) shows the voids formed on the fractured surface of filled samples. From the Figure 8 (a), it is possible to said that the crack is initially generated from the big voids in region 1. In composites system, voids with bigger size tends to accumulate higher stress resulting in the stress concentration site where the point of crack normally begin. Then, the crack propagating to the adjacent area with voids of smaller sizes as in region 2 and 3 marked on the Figure 8 (a). The width of crack propagation path which wider at region 1 and getting narrower at region 3 also indicates the start and end points of the propagation as studied by Zhang et al. [37] on the in-situ observation of crack initiation and growth.

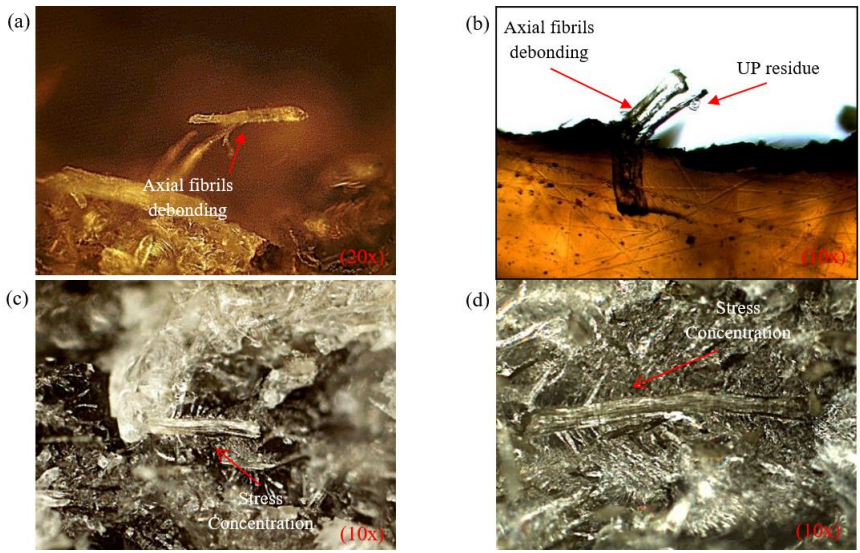


Figure 7: The polarised optical fractographs of (a) and (b) fibril-fibril debonding along the treated fibres on the fractured surface, stress concentration difference between treated (c) TrA and (d) TrB samples observed under the dark and bright field in transmitted and reflected light at 10x and 20x magnifications

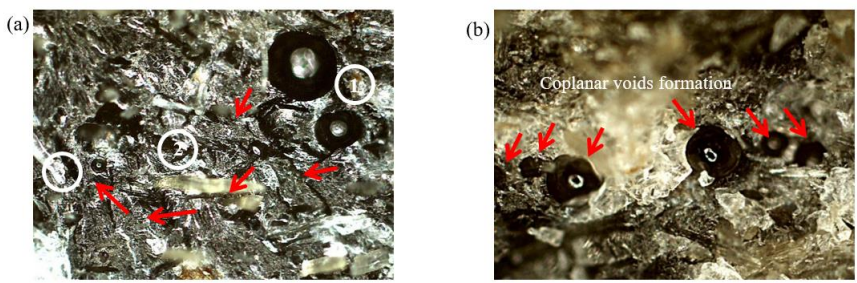


Figure 8. The polarised optical fractographs of (a) crack generation at an area containing voids, and (b) coplanar voids formation on the samples fractured surface observed under dark field in reflected light at 10x magnifications

Figure 9 (a - k) shows the types of fibre failure observed on the surfaces of the fractured surface of untreated and treated sample. Similar types of fibre failure was observed for both untreated and treated samples, including fibre long axial splits at the middle, and fibre edge, fibrillar failure, granular fracture for stepped brake failure, fibre transverse crack (fatigue failure), fibre axial

splits, fibre with diameter reduction and reduce in cross-section, and chemically degraded fibre broke, fibre surface peel off, biaxial failure and mangled fibres shape.

These types of fibre failures might happen due to the fibres' low surface interactions in the fabricated composite system, especially at the inner part of the fibres, which might not expose to the chemical treatments (treated samples), lowering the fibre-matrix interactions. These types of fibre failure might exist since before the sample's fabrication. This is because, the untreated and treated fibre were subjected to the mechanical cutting process to reduce the fibres' size before being fabricated, where the cutting technique caused the variability in the fibres' shape.

In another publication, the fibres' shape was studied after the mechanical cutting process and the same type of fibres's shape were obtained. It can be said that the fibres' shape before the fabrication will also influence the composites reinforcing mechanism, especially at both fibre's ends which will affect the stress accumulation and transfer-ability efficiency. The high irregularities of fibres' end highly affected the deficiency of stress transferability through the samples area. The irregularities of fibres condition may be the cause of the reduction of modulus value of the composite sample as agreed by Schulz [38]. The fibre failure is also related to the decrement in density as discovered in our another publication [39] since voids might be formed at the fibre failure area in the composite system as referred to Figure 9 (l). Hence, after being fabricated in the matrix system, these fibres cannot efficiently absorb the force due to its condition; and failed at lower stress as the fibres.

From the aspect of fibre loading, the dominant failure mode observed for low filler loading samples is fibres debonding. Since the matrix content in low fibre loading samples is higher than the fibre content, there is enough matrix to fully wet the fibres. However, the severity of fibre debonding is higher for the untreated samples since the interfacial adhesion is weaker, as shown in Figure 6 (c). The dominant mode of failure for high filler loading samples is voids formation in the composites system due to the matrix starve, especially at 55% fibre loading, which causes incomplete fibre wetting, as shown in Figure 6 (b). Insufficient fibre wetting and the presence of voids interrupt the flow of stress transfer from the matrix to fibres and fibres to fibres.

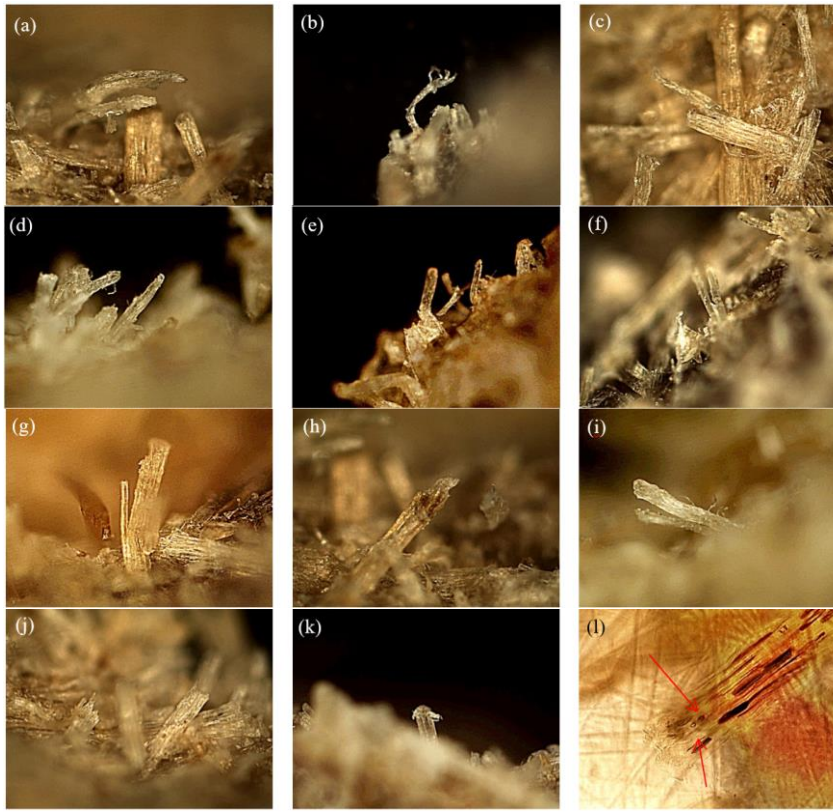


Figure 9: The polarised optical fractographs of fibre failures at the fractured untreated and treated samples surfaces; (a) fibre long axial splits at the middle, and (b) fibre edge, (c) fibrillar failure, (d) granular fracture for stepped brake failure, (e) fibre transverse crack (fatigue failure), (f) fibre axial splits, (g) fibre with diameter reduction and reduce in cross-section, (h) chemically degraded fibre brake, (i) fibre surface peels off, (j) biaxial failure, (k) mangled and (l) voids formation on irregular fibre surface observed under dark field in reflected light with 20x magnifications

Conclusions

This study discusses the influence of fibre length and fibre loading on the flexural properties of untreated and NaOH/Silane treated kenaf/unsaturated polyester composites.

From the aspect of fibre length, despite having the same aspect ratio, the composites with shorter fibres' length exhibited higher specific flexural stress. This is the case for both untreated and treated fibres composites, which might be due to the better stress distribution which enhanced the resistivity of the composites to the applied stress. In a nutshell, it can be said that, even at the same aspect ratio, the reinforcing effect of the fibres with different length can be varied depending on the fibre fraction and interfacial adhesion. The length of the fibres also can influence the stress concentration and stress distribution which will directly affect the properties of the composites.

From the aspect of fibre loadings which are low loadings (5, 10 and 15%) and high loadings (45, 50 and 55%), it can be said that the coalition of chemical treatment gave a positive impact where the specific flexural stress and the specific flexural modulus of treated fibre were higher than the untreated composites for both low loadings and high loadings. This indicates a better adhesion between the kenaf fibre and the vicinity resin, leading to better stress transfer from the matrix to the fibre reinforcement. The treatment of fibre with the NaOH solution had altered the surface topography of the fibre in a way that it had roughened the fibre's surface, which enabled the matrix resin to fill in and create a strong mechanical interlocking, whilst the silanization of the fibre improved the fibre's compatibility with the matrix. This supported by the morphological observation where traces of matrix were observed on the surface of pull-out fibres, indicating a good fibre-matrix adhesion.

Acknowledgement

Authors relay endless gratitude to the Institute of Science and Faculty of Applied Sciences, Universiti Teknologi MARA for providing research materials and facilities and the financial support from the 600-IRMI 5/3/LESTARI (043/2019).

References

[1] M. Akhshik, S. Panthapulakkal, J. Tjong, and M. Sain, "Life cycle assessment and cost analysis of hybrid fiber-reinforced engine beauty cover in comparison with glass fiber-reinforced counterpart," *Environmental Impact Assessment Review*, vol. 65, pp. 111-117, 2017, https://doi.org/10.1016/J.EIAR.2017.04.005

[2] T. Karthik and R. Rathinamoorthy, "Sustainable synthetic fibre production," in *Sustainable Fibres and Textiles*: Elsevier, 2017, pp. 191-240, https://doi.org/10.1016/B978-0-08-102041-8.00008-1

[3] K. Lau, P. Hung, M. Zhu, and D. Hui, "Properties of natural fibre composites for structural engineering applications," *Composites Part B: Engineering,* vol. 136, pp. 222-233, 2018, https://doi.org/10.1016/J.COMPOSITESB.2017.10.038

[4] M. F. Razali, S. A. H. A. Seman, and T. W. Theng, "Effect of fiber misalignment on mechanical and failure response of kenaf composite under compressive loading," *Journal of Mechanical Engineering,* vol. 8, no. 2, pp. 177-191, 2021.

[5] I. Tharazi, A. B. Sulong, and F. Mohd Salleh, "Application of response surface methodology for parameters optimization in hot pressing kenaf reinforced biocomposites," *Journal of Mechanical Engineering,* vol. 17, no. 3, pp. 131-144, 2020.

[6] S. P. Venkatesan, B. V. C. Vignan, and C. A. Reddy, "Study on the properties of natural fibre reinforced polymer matrix composites material," *ARPN Journal of Engineering and Applied Sciences,* vol. 12, no. 24, pp. 7179-85, 2017.

[7] M. N. Yahya and D. D. V. S. Chin, "A review on the potential of natural fibre for sound absorption application," in *IOP conference series: materials science and engineering*, vol. 226, no. 1, 2017, https://doi.org/10.1088/1757-899X%2F226%2F1%2F012014

[8] P. Peças, H. Carvalho, H. Salman, and M. Leite, "Natural fibre composites and their applications: a review," *Journal of Composites Science,* vol. 2, no. 4, p. 66, 2018, https://doi.org/10.3390/JCS2040066

[9] M. M. M. Ghaztar and A. Z. Romli, "The effect of pulverisation process to kenaf fibre physical properties," in *The National Symposium on Polymeric Materials (NSPM)*, Selangor, Malaysia., vol. 1985, no. 1, 2018, https://doi.org/10.1063/1.5047172

[10] F. M. AL-Oqla and M. A. Omari, "Sustainable biocomposites: challenges, potential and barriers for development," in *Green biocomposites*: Springer, pp. 13-29, 2017, https://doi.org/10.1007/978-3-319-46610-1_2

[11] A. Bourmaud, J. Beaugrand, D. U. Shah, V. Placet, and C. Baley, "Towards the design of high-performance plant fibre composites," *Progress in Materials Science*, vol. 97, pp. 347-408, 2018, https://doi.org/10.1016/J.PMATSCI.2018.05.005

[12] F. E. El-Abbassi, M. Assarar, R. Ayad, A. Bourmaud, and C. Baley, "A review on alfa fibre (Stipa tenacissima L.): From the plant architecture to the reinforcement of polymer composites," *Composites Part A: Applied Science and Manufacturing,* vol. 128, 2020, https://doi.org/10.1016/j.compositesa.2019.105677

[13] L. C. Hao, S. M. Sapuan, M. R. Hassan, and R. M. Sheltami, "Natural fiber reinforced vinyl polymer composites," in *Natural Fibre Reinforced Vinyl Ester and Vinyl Polymer Composites*: Elsevier, pp. 27-70, 2018, https://doi.org/10.1016/B978-0-08-102160-6.00002-0

[14] F. Tanasă, M. Zănoagă, C. Teacă, M. Nechifor, and A. Shahzad, "Modified hemp fibers intended for fiber-reinforced polymer composites used in structural applications—A review. I. Methods of modification," *Polymer Composites*, vol. 41, no. 1, pp. 5-31, 2020, https://doi.org/10.1002/PC.25354

[15] S. Dixit, R. Goel, A. Dubey, P. R. Shivhare, and T. Bhalavi, "Natural fibre reinforced polymer composite materials-a review," *Polymers From Renewable Resources*, vol. 8, no. 2, pp. 71-78, 2017, https://doi.org/10.1177/204124791700800203

[16] M. H. Mohammed and B. Dauda, "Unsaturated polyester resin reinforced with chemically modified natural fibre," *IOSR Journal Polymer Textile Engineering*, vol. 1, no. 4, pp. 31-8, 2014.

[17] O. M. L. Asumani, R. G. Reid, and R. Paskaramoorthy, "The effects of alkali–silane treatment on the tensile and flexural properties of short fibre non-woven kenaf reinforced polypropylene composites," *Composites Part A: Applied Science and Manufacturing*, vol. 43, no. 9, pp. 1431-1440, 9// 2012, https://doi.org/10.1016/J.COMPOSITESA.2012.04.007

[18] T. Yu, J. Ren, S. Li, H. Yuan, and Y. Li, "Effect of fiber surface-treatments on the properties of poly (lactic acid)/ramie composites," *Composites Part A: Applied Science and Manufacturing*, vol. 41, no. 4, pp. 499-505, 2010, https://doi.org/10.1016/J.COMPOSITESA.2009.12.006

[19] M. S. Huda, L. T. Drzal, A. K. Mohanty, and M. Misra, "Effect of fiber surface-treatments on the properties of laminated biocomposites from poly (lactic acid)(PLA) and kenaf fibers," *Composites Science And Technology*, vol. 68, no. 2, pp. 424-432, 2008, https://doi.org/10.1016/J.COMPSCITECH.2007.06.022

[20] M. Asim, M. Jawaid, K. Abdan, and M. R. Ishak, "Effect of alkali and silane treatments on mechanical and fibre-matrix bond strength of kenaf and pineapple leaf fibres," *Journal of Bionic Engineering*, vol. 13, no. 3, pp. 426-435, 2016, https://doi.org/10.1016/S1672-6529%2816%2960315-3

[21] M. M. Owen, U. S. Ishiaku, A. Danladi, B. M. Dauda, and A. Z. Romli, "Mechanical properties of epoxy-coated sodium hydroxide and silane treated kenaf /recycled polyethylene terephthalate (RPET) composites: Effect of chemical treatment," in *National Symposium on Polymeric Materials (NSPM) 2018*, Universiti Teknologi MARA, 2018b, p. 27, 2018, https://doi.org/10.1063/1.5047159

[22] M. S. Huda, L. T. Drzal, A. K. Mohanty, and M. Misra, "Effect of fiber surface-treatments on the properties of laminated biocomposites from poly(lactic acid) (PLA) and kenaf fibers," *Composites Science and Technology*, vol. 68, no. 2, pp. 424-432, 2008, https://doi.org/10.1016/J.COMPSCITECH.2007.06.022

[23] A. Orue, A. Jauregi, U. Unsuain, J. Labidi, A. Eceiza, and A. Arbelaiz, "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,* 2016, https://doi.org/10.1016/J.COMPOSITESA.2016.01.021

[24] S. Sreenivasan, S. A. Ibraheem, S. Sulaiman, B. T. Baharudin, M. K. A. Ariffin, and K. Abdan, "Evaluation of combined treatments of natural fibers: kenaf, abaca and oil palm fibers using micromechanical and SEM methods," in *Advanced Materials Research*, vol. 912, pp. 1932-1939: Trans Tech Publ., 2014, https://doi.org/10.4028/www.scientific.net%2FAMR.912-914.1932

[25] M. R. Sanjay, P. Madhu, M. Jawaid, P. Senthamaraikannan, S. Senthil, and S. Pradeep, "Characterization and properties of natural fiber polymer composites: A comprehensive review," *Journal of Cleaner Production*, vol. 172, pp. 566-581, 2018, https://doi.org/10.1016/J.JCLEPRO.2017.10.101

[26] N. N. I. N. I. Ibrahim, "The characterization of glass fibre reinforced unsaturated polyester filled with P84 polyimide / multi-wall carbon nanotubes (MWCNT) hybrid composites," Doctor of Philosophy, Polymer Technology, Industrial Technology, Universiti Teknologi MARA (UiTM), Faculty of Applied Sciences (FSG), 2017.

[27] M. S. Meon, M. F. Othman, H. Husain, M. F. Remeli, and M. S. M. Syawal, "Improving tensile properties of kenaf fibers treated with sodium hydroxide," *Procedia Engineering*, vol. 41, no. 0, pp. 1587-1592, 2012, https://doi.org/10.1016/J.PROENG.2012.07.354

[28] B. F. Yousif, A. Shalwan, C. W. Chin, and K. C. Ming, "Flexural properties of treated and untreated kenaf/epoxy composites," *Materials & Design*, vol. 40, no. 0, pp. 378-385, 2012, http://dx.doi.org/10.1016/j.matdes.2012.04.017

[29] Y. Y. Mohd *et al.*, "Mechanical properties of kenaf polyester composites," *International Journal of Engineering & Technology,* vol. 11, 2011.

[30] D. Cho, H. S. Lee, and S. O. Han, "Effect of fiber surface modification on the interfacial and mechanical properties of Kenaf fiber-reinforced thermoplastic and thermosetting polymer composites," *Composite Interfaces,* vol. 16, no. 7-9, pp. 711-729, 2009, https://doi.org/10.1163/092764409X12477427307537

[31] K. Sever, M. Sarikanat, Y. Seki, G. Erkan, and Ü. H. Erdoğan, "The mechanical properties of γ-methacryloxypropyltrimethoxy silane-treated Jute/polyester composites," *Journal of Composite Materials,* vol. 44, no. 15, pp. 1913-1924, 2010, https://doi.org/10.1177/0021998309360939

[32] *Standard test method for flexural properties of unreinforced and reinforced plastics and electrical insulating materials*, 2010.

[33] D. C. Hylton, "Understanding plastics testing", Hanser Publications, 2004.

[34] *Standard practice for characterization of particles*, 1998 (Reapproved 2003).

[35] M. M. M. Ghaztar, N. N. I. N. Ibrahim, and A. Z. Romli, "The effect of viscosities of various coating solutions on the physical, mechanical and morphological properties of kenaf/ epoxy composites," *Journal of Biointerface Research in Applied Chemistry*, vol. 10, no. 3, pp. 5660 - 5664, 2020, https://doi.org/10.33263/briac103.660664

[36] H. Kaco, M. S. S. Sajab, S. Zakaria, and C. C. Hua, *Potential of advanced green products from agricultural biomass sources*. Universiti Kebangsaan Malaysia (UKM), Selangor, Malaysia.: Penerbit Universiti Kebangsaan Malaysia (UKM), p. 173, 2018

[37] S. Sreenivasan, S. A. Ibraheem, S. Sulaiman, B. T. H. T. Baharudin, M. K. A. Ariffin, and K. Abdan, "Evaluation of Combined Treatments Of Natural Fibers: Kenaf, Abaca and Oil Palm Fibers Using Micromechanical and SEM Methods," *Advanced Materials Research*, 2014, https://doi.org/10.4028/www.scientific.net%2FAMR.912-914.1932

[38] E. Schulz, *Fibre failure and wear of materials. An atlas of fracture. Fatigue and durability*. (Acta Polymerica, no. 4). Akademie Verlag GmbH, pp. 192-192, 1991, https://doi.org/10.1002/actp.1991.010420418

[39] M. M. M. Ghaztar, N. N. I. N. Ibrahim, and A. Z. Romli, "The relationship between hardness to the tensile properties of kenaf/ unsaturated polyester composite," in *Advance Materials Conference (AMC 2016)*, Langkawi, Malaysia., vol. 1901, 2017, https://doi.org/10.1063/1.5010466