Effects of Mercerization on the Properties of Paper Produced from Malaysian Pineapple Leaf Fiber

Nadirul Hasraf Mat Nayan, Saiful Izwan Abd Razak, Wan Aizan Wan Abdul Rahman* and Rohah Abd Majid.
Polymer Engineering Department, Faculty of Chemical Engineering, Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia

***Abstract*— Environmental awareness and depletion of the wood resources are among vital factors that motivate various researchers to explore the potential of agro-based crops as an alternative source of fiber material in paper industries such as writing, printing, wrapping, and packaging. Fibers from agro-based crops are available in abundance, low cost, and most importantly its biodegradability features, which sometimes referred as "ecofriendly" materials. This paper reports the effects of mercerization (NaOH treatment) on the properties of pineapple leaf fiber (PALF) pulp and paper. The individual fibers were characterized having good tensile properties at 15% NaOH treatment and favourable structural properties as characterized by Fourier transform infra-red (FTIR) spectroscopy and X-ray diffractometer (XRD). It was also shown that the PALF paper achieved desirable tear index value and uniform morphological observations at 15% NaOH concentration. This type of chemical treatment is useful to obtain PALF based paper products.**

***Index Term*— Pineapple leaf fiber; Fiber modifications; Mercerization; Paper; Pulp; Tear index**

I. INTRODUCTION

Present-day, the center of research in the field of paper science and technology has been aimed on developing papers for writing, printing, wrapping, packaging, and many other paper products from renewable resources, mostly the abundantly available agro-waste and lignocellulosic materials. A vast number agro-waste and lignocellulosic materials that have both economic and environmental benefits are being considered for application in pulp and paper industries. Growing environmental awareness and depletion of the wood resources worldwide are among the vital factors that motivated academia to explore the potential of agro-waste crops and lignocellulosic materials as the alternative source of fiber material in pulp and paper industries. Within the past few years, there has been a tremendous increase in the use of natural fibers as source of fiber for pulp and paper [1]. The potential of natural fiber based paper using jute, kenaf, hemp, coir, sisal, pineapple, etc., has received numerous attentions among researchers worldwide for their excellent specific properties [2]. Therefore, the availability of abundantly inexpensive lignocellulosic natural fibers, such as pineapple leaf fiber (PALF) in tropical countries, such as Malaysia, provides a unique opportunity of exploring the possibility of its utilization as an inexpensive raw material for pulp and paper applications.

PALF are leaves of the plant, *Anannus comosus*, originating to the Bromeliaceae family. The pineapple plant has a very short stem which first produces a rosette of leaves but which latter elongated and bears numerous spirally arranged fibrous leaves. The leaves are sword shaped and approximately 3 feet long, 2 to 3 inch wide [3]. In addition, the leaves are dark green in colour and bear spines of claws on their margins. The leaves of the pineapple plant yield strong, white fine silky fibers [4]. The fibers are obtained by either mechanical means or retting the leaves in water. Fresh leaves yield about 2 to 3% of fiber [5]. Pineapple is largely cultivated in Malaysia, mainly for its fresh consumption, canning and juicing. Its cultivation in Malaysia is substantial and in 2010 alone about 25, 100 hectares of land is cultivated [6]. From the Food Agriculture Organization (FAO) online database, with 648, 193 metric tonnes or 5.3% of the world pineapple production, Malaysia currently stood at the ninth position for the production and its export to the world market. Generally, there are numerous Malaysian varieties of pineapple, but the one that caught attention and preferable among the majority of farmers is the Josapine variety [7]. This pineapple variety was introduced almost a decade ago by Malaysian Agricultural Research and Development Institute (MARDI) and since then it had been commercialized successfully. However, with increasing pineapple production, pineapple wastes, are also proportionally increasing. Waste disposal raises a growing concern since it is usually prone to microbial spoilage and it causes serious environmental problems. The utilization of waste, such as PALF, would provide an innovation to handle the great deal of waste from processing.

Chemically, PALF is multicellular lignocellulosic in nature. The major constituents of PALF comprises of mainly cellulose

The corresponding author can be contacted via e-mail: *w.aizan@cheme.utm.my

(70-82%), hemicellulose (10-16%), and lignin (5-12%) [8]. Due to its high cellulose content, PALF exhibits superior mechanical properties [9]. PALF is of fine quality, and unlike jute, its structure is without mesh [10]. It has a ribbon-like structure and is cemented together by gummy matters known as lignin, which contribute to the strength of the fiber [11]. On the other hand, PALF filaments are well separated and it is two and half times more extensible, with superior fiber bundle strength [12]. However, although PALF are known to have excellent specific properties as mentioned before, majority of these pineapple leaves are still going to waste because of lack of knowledge about their economic applications. Therefore, profound research has to be done to discover the potential applications of PALF, and one way to utilize this natural resource is to convert it into pulp and paper.

Mercerization or sometimes referred to as alkali treatment is the process of subjecting a cellulose fiber to an interaction with a relatively concentrated aqueous solution of a strong base [13], with the objective of producing sufficient swelling, thus, resulted in a reduction of linear density, shrinkage in dimension and more visible fibrillar structure of a fiber, as well as change in mechanical properties considerably depending on the treatment time and concentration of alkali solution. For cellulose fibers, hemi-cellulose has shown to be very sensitive to the action of caustic soda, which exerts only a slight effect on lignin or cellulose [14]. The effects of mercerization on the suitability to mechanical treatment, prominent tensile strength, of cellulose fibers have been extensively studied. From previous research, it was reported that chemically modified PALF with alkali treatment of caustic soda leads to a significant increase in tensile strength when compared to other techniques [15].

This study reports the effect of caustic soda solution (NaOH) concentration on the tensile strength, FTIR spectroscopy and XRD properties of Malaysian PALF (*Ananas Comosus*, Josapine Hybrid). Its paper properties were characterized as well which include tear index and morphological characteristic.

II. EXPERIMENTAL

The materials used for the study includes PALF, collected from FIMA pineapple plantation estate in Ayer Baloi district of Pontian province, Malaysia, and caustic soda (NaOH), obtained from Merck. Each leaf was individually separated and cleaned by hand, and then stored at temperature of 4 °C in a refrigerator, prior to use. PALF were chopped into uniform size of approximately 10 cm. The fibers were treated with 10%, 15% and 20% NaOH aqueous solution (w/v) in beakers and continuously stirred for a period of 24 h at room temperature. The mercerized fibers were washed several times with distilled water followed by washing with 1% HCl solution to neutralize the remaining alkali and rinsing with distilled water. The PALF pulp was formed into paper sheets by hand and conditioned at 23^{o}C and 50% RH for at least 24 h before testing. As for fiber testing, the treated PALF were dried in a vacuum oven at temperature of 60 °C for 24 h and then further dried in a drying oven at 100 °C for 1 h.

The fiber bundle tensile tests were performed using an Instron Tensile Testometric machine with crosshead speed of 1mm/min at room atmosphere of 23 °C. The un-mercerized and mercerized PALF were cut into 60 mm lengths and separated into individual fiber bundle. The gauge length was approximately 25 mm. 15 replications were done for each fiber type. The gripping technique was in accordance to ASTM D3822. The unit break (N/mm^2) is calculated using F/A; where, F is the maximum breaking load and A is the cross sectional area of the fibers. FTIR spectra of the fibers were obtained from KBr disc of samples using a Perkin Elmer infrared spectrometer with a resolution of 0.4 cm^{-1}. The X-ray diffraction profiles of the fibers were obtained by using Cu Kα radiation (λ = 0.154 nm), generated with Philips diffractometer (45 kV, 100mA) at scanning rate of 0.02s^{-1} in the 2θ range from 2 to 90°. The crystalline index of cellulose, C_{Ir} was calculated using (I_{002} – I_{am}/I_{002}) x100, where, I_{002} is the peak intensity of cellulose I (C_I) and I_{am} is the peak intensity of the amorphous fraction. Tear indexes of the PALF paper sheets were tested according to TAPPI standard test. The structure and morphology of the PALF papers were observed by using a scanning electron microscope (SEM), Philips XL40, at an accelerating voltage of 10 kV followed by elemental analysis using energy dispersive X-ray (EDX) on the sheets surface.

III. RESULTS AND DISCUSSION

A. *Fiber Properties*

Tensile strength of the un-mercerized PALF corresponds well with previously reported works [16, 17]. As shown in Fig. 1, the 10% mercerized PALF exhibits better tensile properties than the un-mercerized PALF. Treatment with NaOH increases the tensile strength of the mercerized PALF due to the removal of impurities and partial removal of surface hemicelluloses and lignin. The mercerized PALF shows a maximum tensile strength at 15% NaOH treatment. However the value reduced tremendously when the concentration increased to 20%, which is lower compared to that of un-mercerized PALF. This can be attributed to the fibers deterioration and rupture at high NaOH concentration that might reduced the PALFs' tensile properties. The mercerization process of the PALF surface is depicted in Fig. 2.

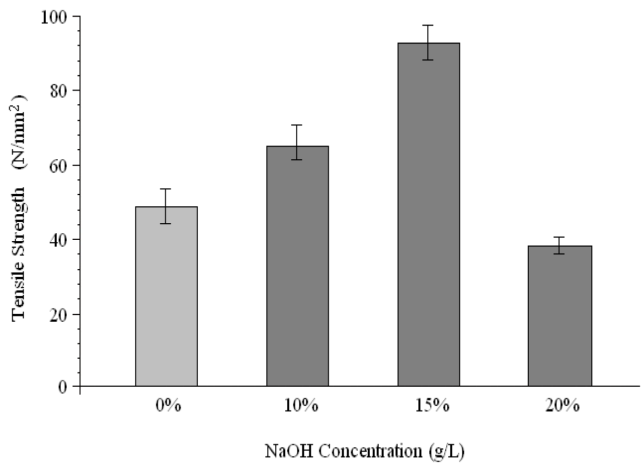

Fig. 1. Tensile strength of un-mercerized and mercerized PALF at different NaOH concentrations

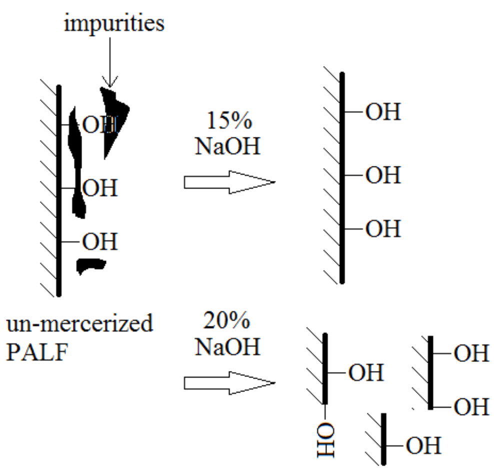

Fig. 2. Schematic diagram of the mercerization treatment.

The FTIR characteristic features of the PALF samples (Fig. 3) are due to its lignocellulosic components [18]. The FTIR pattern of un-mercerized PALF (Fig. 3a) shows strong broad peak at 3200-3600 cm^{-1}, which is the characteristics of hydrogen-bonded OH stretching vibrations, correspond to the intermolecular and intramolecular H bond of free OH of cellulose [19]. The strong peak at 2900 cm^{-1} represents the CH stretching vibrations [20]. The peak at 1730 cm^{-1} is the characteristic band for carbonyl (C=O) stretching that represents the ester linkage of lignin and acetyl group of hemicelluloses. It is noticeable that the 10% NaOH treated PALF (Fig. 3b) revealed no distinct peak of carbonyl stretching (1730 cm^{-1}). It can be said that during mercerization process, a substantial portion of uranic acid, a constituent of hemicellulose xylan, is removed [16], resulting in the disappearance of this peak. Similarly, it can be noted that there is a peak in un-mercerized PALF at 1245cm cm^{-1} which no longer exists in the mercerized PALF sample. This band represents the stretching of aryl group in lignin. This indicates that the removal of lignin was achieved. Spectrum of 15% NaOH treated PALF (Fig. 3c) shows similar pattern with the 10% NaOH treated PALF. Spectrum of 20% NaOH treated PALF (Fig. 3d) on the other hand revealed more intense OH stretching vibrations. This can be associated with the rupture and deterioration of fibers than open up more surface hydroxyl groups as illustrated earlier in Fig. 2.

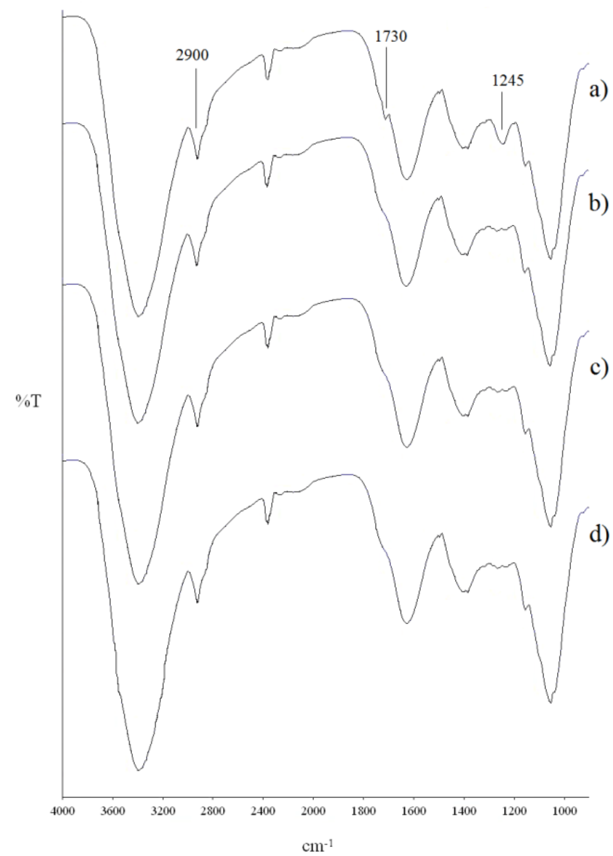

Fig. 3. IR spectra of a) un-mercerized, b) 10, c) 15 and d) 20% mercerized PALF.

Fig. 4 shows the XRD diffractograms of the un-mercerized and mercerized PALF with different NaOH concentrations. All the PALF specimens revealed crystallinity peak of native cellulose, the C1 peaks (2θ = 23.0, 002 plane) [21]. It can be observed that the C1 peak of un-mercerized PALF (Fig. 4a) exhibits lower peak intensity compared to that of its' amorphous peak. Major portion of the sample is covered by amorphous lignin and hemicellulose that inhibits the diffraction of the cellulose component. Thus C_{Ir} value for the un-mercerized PALF is not available. Meanwhile C_{Ir} for 10 and 15% mercerized PALF (Fig. 4b and c) are found to be 53.8 and 62.5%, respectively. This clearly demonstrates the increase in the degree of crystallinity of PALF after removal of unwanted impurities. Furthermore, no new peaks are observed for the 10 and 15% mercerized PALF. This shows that no crystalline transformation of PALF structure occurred with NaOH treatment. However, an increase in the NaOH concentration up to 20% (Fig. 4d) reduced the C1 peak reaching an intensity value equal to that of its' amorphous peak. This is may be due to high concentration of NaOH which reduces the crystallinity of cellulose.

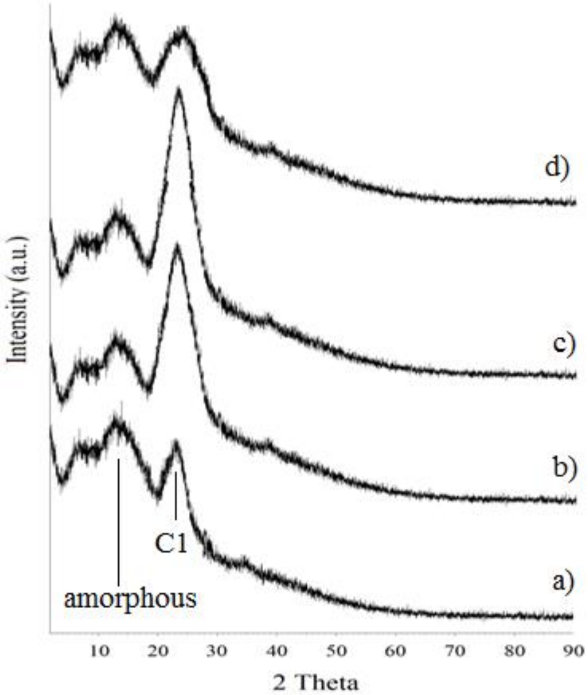

Fig. 4. XRD profiles of a) un-mercerized, b) 10, c) 15 and d) 20% mercerized PALF.

B. *Paper Properties*

Fig. 5 shows the photograph of PALF paper at various treatments. The differences in colors are associated with the presence of conjugated lignin compound [19]. The untreated PALF paper (dark green) changes its color as the NaOH concentration increases. This signifies that the conjugated compounds are removed which lead to PALF with brighter color. Tear indexes of the PALF papers are shown in Fig. 6. The un-mercerized PALF paper shows the lowest tear index. This is due to the poor paper formation of the fibers caused by the unremoved surface lignin and impurities which lead to poor tearing resistance. 10% mercerized PALF paper significantly increases the tear index up to two fold followed by maximum value for the 15% treated PALF paper. This proves that treatment with NaOH provide desirable paper formation with good mechanical properties. At high NaOH concentration (20%), tear index of the paper reduced. Breakage and ununiformity of fibers might cause this to happen.

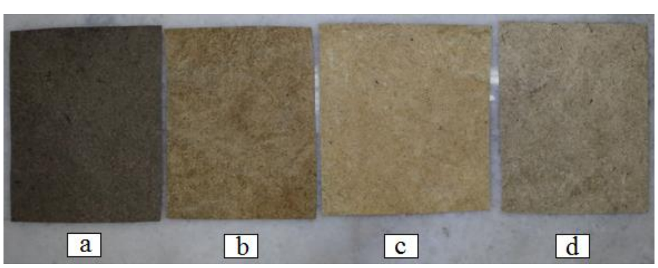

Fig. 5. PALF paper of a) un-mercerized, b) 10, c) 15 and d) 20% mercerized.

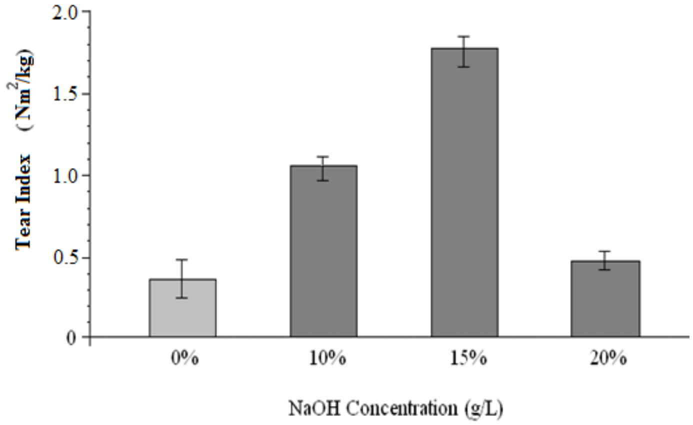

Fig. 6. Tear index of un-mercerized and mercerized PALF paper at different NaOH concentrations.

SEM observation of Fig. 7a shows the morphology of un-mercerized PALF paper. The surface is fully covered with lignin and impurities, no distinct fibers can be seen. This correspond well with the its dark green color feature (Fig. 5a) and low tear index value (Fig. 6). Furthermore the EDX spectrum of the sample (Fig. 8a) detects significant presence of magnesium and potassium atoms which represent ash and impurities content of the untreated fibers. 10 and 15% mercerized PALF paper (Fig. 7b and c) show clear presence of fiber with the lignin binding component in the background. As it can be observed, the 15% mercerized PALF paper revealed more uniform texture compared to that of 10% mercerized PALF paper. Good uniformity will avoid weak spots during mechanical testing. This corroborates the higher tear index for 15% treated paper compared to that of 10% treated paper. Their EDX spectra (Fig. 8b and c) indicate good carbon to sodium atom ratio and no significant impurities atoms present, which means that residual sodium ions from the mercerization and impurities had been sufficiently removed. Morphology of the 20% mercerized PALF paper (Fig. 7d) shows fiber breakage and rupture due to high concentration of NaOH. The high content of sodium atom can be seen in the EDX spectrum of Fig. 8d.

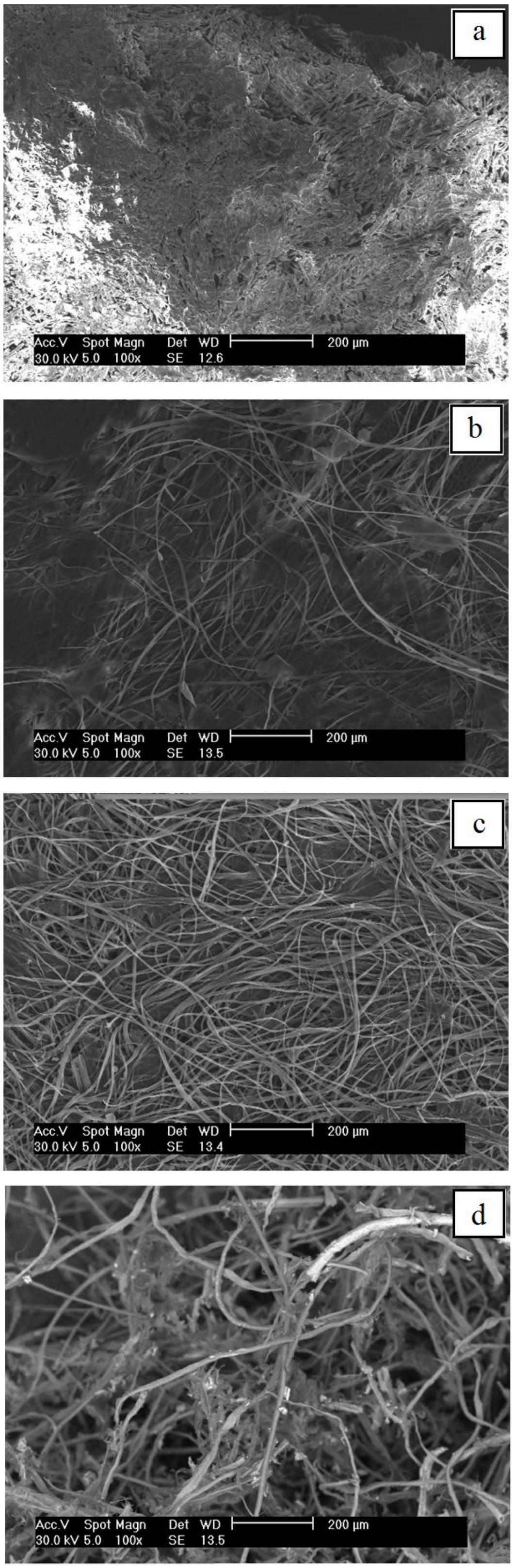

Fig. 7. SEM images of PALF paper a) un-mercerized, b) 10, c) 15 and d) 20% mercerized.

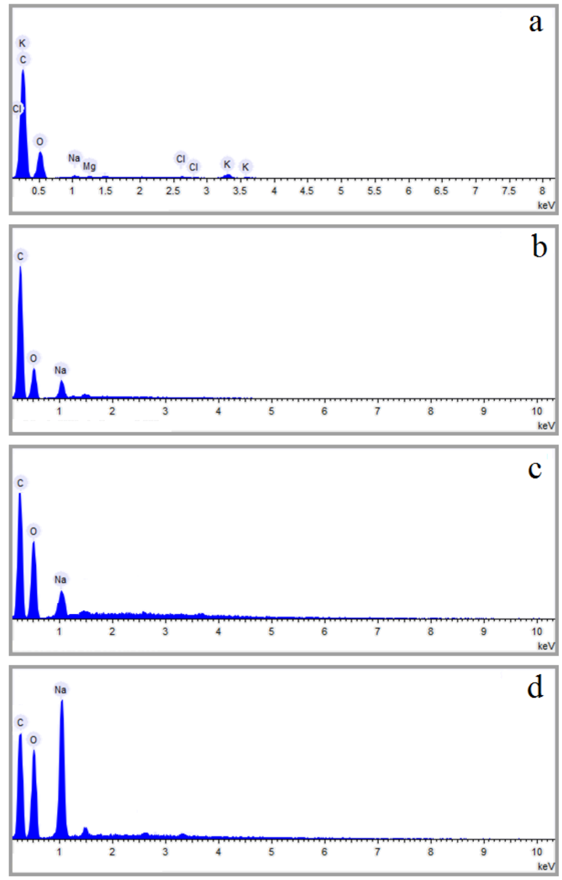

Fig. 8. EDX spectra of PALF paper a) un-mercerized, b) 10, c) 15 and d) 20% mercerized.

IV. CONCLUSIONS

PALF were treated with different concentrations of NaOH solution and were formed into handmade paper sheets. It was observed that NaOH treatments have significant influence on the fiber properties even at 10% NaOH concentration. Fiber bundle tensile test, IR spectroscocpy and XRD revealed that 15% NaOH had the most positive effects on the PALF properties. PALF paper of the 15% mercerized pulp showed similar effect with good tear index and uniform surface topography. Meanwhile PALF treated with high NaOH concentration (20%) reduced the fiber and paper properties. Findings of this work indicated that Malaysian PALF shows promise to be used as source of pulp in papermaking via chemical treatment such as mercerization.

ACKNOWLEDGMENT

The financial support provided by the Universiti Teknologi Malaysia through RUG grant is gratefully acknowledged.

REFERENCES

[1] S. J. Eichhorn, C. A. Baillie, N. Zafeiropoulos, L. Y. Mwaikambo, M. P. Ansell, and A. Dufresne, J. Mater. Sci., 36 (2001) 107–119.
[2] F. Nagota, and H. Takahashi, Compos. Eng., 5 (1995) 743-752.
[3] M. Misra, A. K. Mohanty, and L. T. Drzal, Polym. Mater. Sci. Eng., 85 (2000) 299–310.
[4] A. K. Bledzki, S. Reihmane, and J. Gassan, J. Appl. Polym. Sci., 59 (1996) 329-338.
[5] R. K. Samal, and M. Bhuyan, J. Appl. Polym. Sci. 52 (1994) 675-685.

[6] R. M. N. Arib, M. S. Sapuan, M. A. M. M. Hamdan, and H. M. D. K. Zaman, Polym. Compos., 12 (2010) 341-348.
[7] A. V. Tran, Ind. Crop. Prod., 24 (2006) 66-74.
[8] S. Mishra, A. K. Mohanty, L. T. Drzal, M. Misra, and G. Hinrichsen, Macromol. Mater. Eng., 48 (2004) 285–290.
[9] L. U. Devi, S. S. Bhagawan, and S. Thomas, J. Appl. Polym. Sci., 64 (1997) 739–748.
[10] J. Gassan, and A. K. Bledzki, J. Appl. Polym. Sci., 71 (1999) 623–629.
[11] S. Mishra, M. Misra, S. S. Tripathy, S. K. Nayak, and A. K. Mohanty, J. Reinf. Plast. Compos., 20 (2001) 321-337.
[12] M. Das, A. Pal, and D. Chakraborty, J. Appl. Polym. Sci., 100 (2006) 238–244.
[13] S. Luo, and A. N. Netravali, Polym. Compos., 20 (1999) 367–378.
[14] W. Liu, M. Misra, P. Askeland, L. T. Drzala, and A. K. Mohanty, Bioresource Technol., 46 (2005) 710–721.
[15] R. K. Samal, and M. C. Ray, J. Appl. Polym. Sci., 64 (1997) 119–125.
[16] A. K. Mohanty, M. Misra, and L. T. Drzal, Polym. Polym. Compos., 86 (2002) 341-353.
[17] J. George, S. S. Bhagawan, and S. Thomas, Compos. Interf., 19 (2012) 793–810
[18] R. K. Samal, and M. Bhuyan, J. Appl. Polym. Sci., 52 (1994) 675-685.
[19] S. I. A. Razak, W. A. W. A. Rahman, S. Hashim, and M. Y. Yahya, Compos. Interf., 19 (2012) 365-376.
[20] V. L. Chiang, H. J. Cho, R. J. Puumala, R. C. Eckert, and W. S. Fuller, Tappi J., 70 (1987) 101-104.
[21] S. Park, J. O. Baker, M. E. Himmel, P. A. Parilla, and D. K. Johnson, Biotechnol. Progr., 3 (2010) 1–10.