MORPHOLOGICAL AND CHEMICAL NATURE OF FIBER STRANDS OF OIL PALM EMPTY-FRUIT-BUNCH (OPEFB)

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In this work we examined the morphological and chemical characteristics of the fibrous strands of oil palm empty-fruit-bunch which were left behind after being stripped of their fruits used for oil production. The empty-fruit-bunches were mechanically loosened to yield the fibrous strands, which can be used in paper and board making. We found that the fibrous strands had unique structure by having several large-diameter, long vessel elements in their core region, surrounded by vascular fibers. They had numerous silica-bodies attached to craters on their surfaces; the craters were perforated at the bottom. Many other minerals were also present in the strands. Our microscopic observations suggested that the silica-bodies are connected to a network of siliceous pathway within the fibrous matrix, and minerals tend to concentrate adjacent to the silica-bodies. Our findings could be useful in identifying suitable techniques for processing the oil palm fiber strands into value-added products.

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INTRODUCTION

Oil palm, *Elaeis guineensis* (Fig. 1), is one of the most economical perennial oil crops for its valuable oil-producing fruits in tropical regions such as West Africa (Khozirah and Khoo 1991) and Southeast Asia. In Malaysia alone large amounts of oil palm biomass are generated by the palm oil industry, for example 5000 million tonnes (green) of felled trunk in 2000 (as projected by Husin et al. 1986), 36 million tonnes (odmt) per year of fronds from pruning and replanting (Wan Zahari et al. 2004) and 5.2 million tonnes (odmt) per annum of empty-fruit bunches (EFB) in 2002 (Tanaka and Yamamoto, 2004).

In the oil extraction process the fruits or nuts are first stripped from fruit bunches, leaving behind the empty-fruit bunches as waste. The abundance of oil palm empty-fruit-bunches (OPEFB) has created an important environmental issue such as fouling and attraction of pests. However, valuable fiber can be obtained from the OPEFB for manufacturing board and paper, for example. The OPEFB, nonwoody lignocellulosic material, is rather complicated in terms of cell type, morphology and chemical composition. Albeit its approximate chemical constituents have been reported before (Khoo, et al., 1991; Mansor and Ahmad, 1991; Jalil et al., 1991; Law and Jiang, 2001),

the physical and chemical nature of the fibrous strands prepared from OPEFB has not been investigated in detail. Such knowledge on this biomass is of great importance relative to its industrial processing and potential utilization in value-added products, mitigating the environmental concerns mentioned earlier.

The objective of this work was to characterize the physical nature of the fibrous strands of OPEFB, quantify the organic and inorganic components in OPEFB and examine techniques that can remove the problematic constituents in view of possible use of OPEFB in paper and other products.

EXPERIMENTAL

Material

The fibrous strands of OPEFB (Fig. 1, right) used in this study were obtained from an oil palm mill in Malaysia. The OPEFB was mechanically treated to loosen the fibrous strands, which were washed, cleaned, sorted, and air-dried.

Fig. 1. Photographs showing oil palm tree (left), fruit bunch (center), and fibrous strands (right)

Methods
Fiber morphology measurements

Physical properties such as fiber diameter and cell-wall thickness were determined using 40-µm-thick cross-sections of the fibrous strands and a transmission light microscope (Zeiss Photomicroscope III). The cross-sections were prepared from the fibrous strands embedded in paraffin prior to microtoming. Some fibrous strands were macerated in a solution containing equal volumes of hydrogen peroxide and acetic acid, at 70 °C, for about 3 h or until the fibers became readily separable by a gentle mechanical stirring. Fiber morphology data were obtained by means of a Fibre Quality Analyzer (FQA, OpTest Inc., Canada).

The chemical characteristics were determined using TAPPI test methods: lignin (T 222), holocellulose (T 222), hot-water solubility (T 207), 1% NaOH solubility (T 212), alcohol-benzene solubility (T 204), dichloromethane (DCM) solubility (T 204), and ash (T 211, T 266).

Elemental analyses and microscopy

Analysis of the elements in samples was carried out by means of LEO SUPRA 55VP scanning electron microscope (SEM) interfaced with energy dispersive analysis of X-ray (EDAX).

RESULTS AND DISCUSSION

Physical Characteristics

In cross-sectional view one can observe usually three large vessel elements in the core region of a vascular bundle (Fig. 2, left, top). These highly pitted vessel elements are clearly shown in longitudinal view (Fig. 2, right-top). Fibers and vessels of various sizes are presented in the bottom-right photograph of Fig 2. Physical characteristic of the fibrous elements are shown in Table 1. In comparison with those from a Canadian trembling aspen, the OPEFB fibers have similar length cell diameter but much thicker cell wall and, as a result, higher coarseness and rigidity index. Consequently, they yield paper with higher bulk or lower sheet density and inferior tensile strength when compared to paper made from aspen fibers (Law and Jiang, 2001). However, due to the presence of the particularly long vessel elements, they give considerably high tear index. Noteworthily, granules of starch are found in the interior of the vascular bundle (Fig. 2. left, bottom); their presence was identified using an iodine solution.

Table 1. Fiber Properties

Property	OPEFB fiber	Aspen fiber
Length-weighted fiber length, mm	0.99	0.96
Fiber diameter (D), μm	19.1	20.8
Cell-wall thickness (T), μm	3.38	1.93
Fiber coarseness, mg/m	1.37	1.01
Fines (<0.2 mm), % (arithmetic mean)	27.6	18.1
Rigidity index, $(T/D)^3 \times 10^{-4}$	55.43	7.99

Chemical Constituents

The chemical constituents in OPEFB are presented in Table 2. Note that differences in magnitudes exist in comparison with the findings of other researchers. These variations could arise depending on the sources of raw material and on the historic treatments the material had received prior to laboratory analyses. The extent of pre-treatment such as washing, a standard process step, could influence significantly water-soluble and 1% NaOH-soluble components. The content of acid-insoluble lignin, which has poor solubility in water, is comparable to those reported by other workers (Khoo and Lee, 1991, Law and Jiang, 2001) and is similar to that of most common hardwood species (Berzins, 1966).
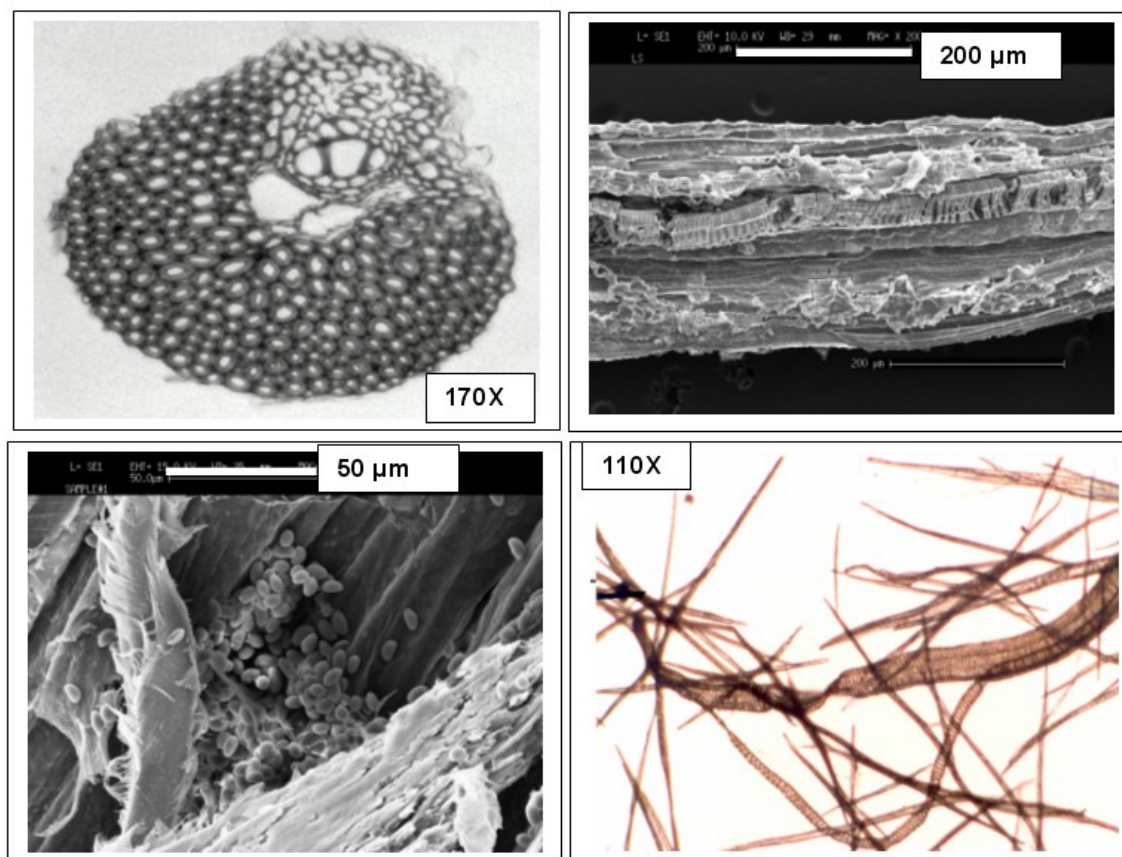
Fig. 2. Cross-section view of a fibrous strand (left, top, 170X), longitudinal view (right, top), interior view showing starch granules (left, bottom), and fibrous elements (right, bottom, 110X).

In addition to its organic component the OPEFB is rich in inorganic elements (Table 2). The presence of silica and other metals could complicate pulping and bleaching of this raw material. Silica is harsh on treatment equipment and complicates the recovery of spent liquor (Pan and Learly, 2000; Kulkarni et al., 2005; Tutus and Eroglu, 2003). Metals in raw material can interfere with pulping and bleaching chemicals, particularly in processes where hydrogen peroxide is used (Prasakis et al., 1996; Heikkila and Vuorinen, 2000; Zhao et al., 1992; He et al., 2003).

Surface Characteristics of OPEFB Strand

Silica-bodies are found in great number on OPEFB strand (Fig. 3, left). They attach themselves to circular craters which are spread relatively uniformly over the strand's surface. The round-shaped spiky silica-bodies measure about 10-15 µm in diameter. These bodies are not detectable with EDAX or seen under SEM at the interior (Fig. 3, right). However, minute pit-like conduit-openings are observable at the interior; they might probably be the siliceous pathways connecting the interior to the surface. The silica-bodies (Fig. 4, top) are hard but can be dislodged mechanically, e.g. hammering the OPEFB strands in a Ziplock LDPE bag with a Staccato Hammer.

The shape, size and distribution pattern of silica bodies observed on fiber strands of OPEFB of *Elaeis guineensis* are strikingly similar to those in the epidermis of oil palm leaf (*Syagrus coronata*) as reported by Lins et al (2002). These researchers also reported that silicon and oxygen are two elements present in the silica bodies.

The deposition of silica bodies in biologically well engineered craters is a unique feature, contrasting with the usual extra- and intra-cellular silica deposition (Neumann and De Figueiredo, 2002; Richmond and Sussman, 2003). The presence of well engineered craters with perforated bottoms (Fig. 4) suggests that the deposition of silica on fiber strand surfaces is a predetermined biological process, not a random occurrence. Such genetic arrangement underscores the biological need of oil palm trees, the purpose of which, speculatively, might be multifunctional and beyond the nutritional requirement,

Table 3 shows the changes in silica content after mechanical treatment (hammering) and washing. Hammering reduced the silica content by 11.1% or 12.9% when adjusted to the yield of 98%. The action of hammering and washing combined gave greater loss in silica, 22.2% or 26.6% when the final yield of 94% was taken into account. Note that, for the hammered sample, the EDAX gave higher, about two fold, silica content than the TAPPI method did. This difference is suspected to come from variation in sample homogeneity, since no such difference occurred in the hammered and washed sample, as shown in Table 3.

Table 2. Chemical Constituents in OPEFB

| Constituent	% of dry OPEFB	Reference	
		Khoo & Lee 1991	Law & Jiang 2001
Extractives	3.7 ± 0.3	0.9	2.8
Acid-insoluble lignin	18.8 ± 0.3	17.2	17.6
Ash-free acid-insoluble lignin	17.8 ± 0.2	-	-
Ash	1.3 ± 0.2	0.7	3.8
Hot-water soluble	7.5 ± 0.8	2.8	9.3
1% NaOH soluble	14.5 ± 2.7	17.2	29.9
Holocellulose	82.4 ± 1.4	70.0	86.3
Cellulose	62.9 ± 2.0	42.7	-
Hemicellulose	28.0	32.5 (Leh, 2002)	-
Arabinose	2.5 ± 1.1	-	-
Xylose	33.1 ± 2.6	-	-
Mannose	1.3 ± 0.01	-	-
Galactose	1.0 ± 0.0	-	-
Glucose	66.4 ± 3.7	-	-
		Singh et al.,	1999
Silica (EDAX)	1.8 (atomic)	-	
Silica (TAPPI method)	0.9 ± 0.1		
Copper	0.8 ± 0.7 g/g	23 mg/L	
Calcium	2.8 ± 0.1 g/g	0.25% (CaO)	
Manganese	7.4 ± 0.4 g/g	48 mg/L	
Iron	10.0 g/g*	473 mg/L	
Sodium	11.0 ± 0.4 g/g	-	

* Only found in one sample
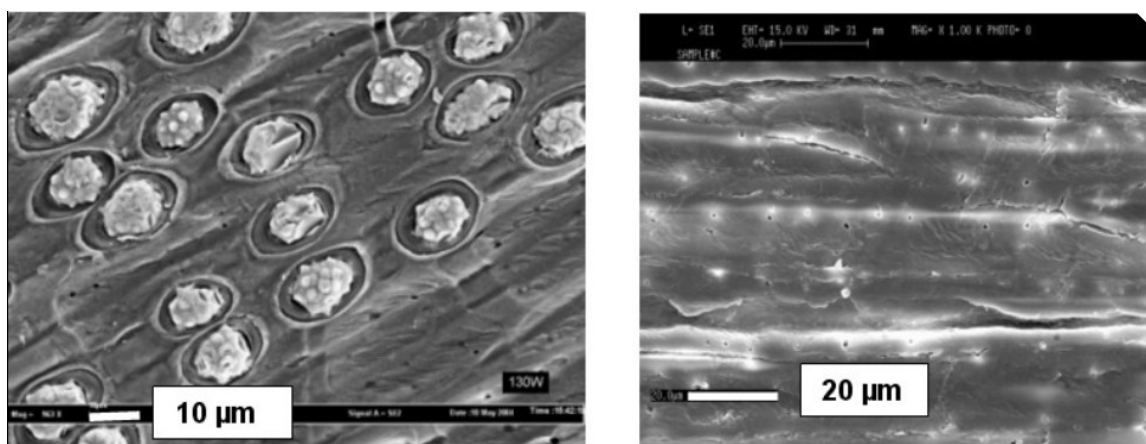
Fig. 3. Surface of OPEFB strand with silica bodies (left) while the interior is lack of visible silica bodies (right).

The removal of silica-bodies revealed that the bottom of the silica-crater is perforated (Fig. 4, bottom), which could suggest that the formation of silica might have originated from the interior of the fibrous strand through the probable siliceous pathways mentioned above. It is, however, unclear at this point whether the perforations are intra-cellular or extra-cellular in nature. However, the removal of silica-bodies would enhance chemical penetration in pulping.

Table 3. Effect of Mechanical Treatment on Silica Content

Silica	Amount in treated o.d. OPEFB	*Change %	
		Raw	Corrected**
TAPPI method	0.8 %	- 11.1	- 12.9
EDAX	1.3 % (Atomic)	- 27.8	- 29.2
Yield	98 %		

* Relative to untreated OPEFB
** Corrected for yield

Table 4. Combined Effect of Hammering and Washing on Silica Content

Silica	Amount in treated 0.d. OPEFB	*Change %	
		Raw	Corrected**
TAPPI method	0.7 %	- 22.2	- 26.6
EDAX	0.7 % (Atomic)	- 61.1	- 63.3
Yield	94 %		

* Relative to untreated OPEFB
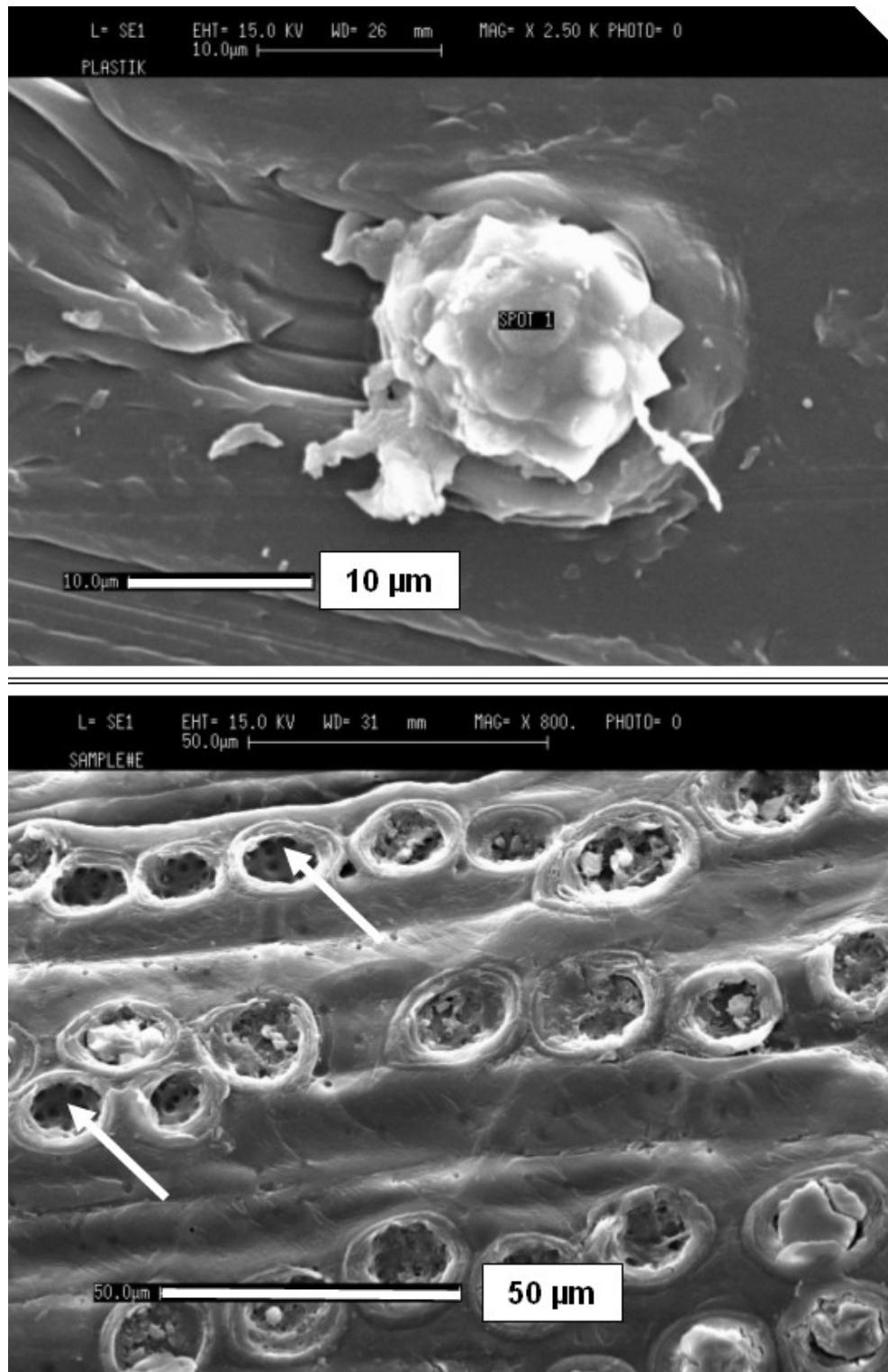** Corrected for yield

Fig. 4 . A dislodged silica-body attached to plastic film (top). Perforations at bottom of silica-body craters (bottom, arrows).

Minerals in OPEFB Strand

As stated earlier, hydrogen peroxide can be decomposed by the minerals present in the raw material to be processed, deactivating its chemical efficiency. Hence, in pulping or bleaching that involves the use of hydrogen peroxide, it is essential to sequester these minerals beforehand. Here, we studied the combined effect of hammering-washing-DTPA (diethylenetriaminepentaacetic acid) treatment on mineral content in OPEFB strand. The idea of DTPA treatments was to remove soluble minerals from OPEFB strand and to deactivate the non-acid-soluble minerals, as these were potential hindrance of efficient peroxide pulping or bleaching system. The results are presented in Table 5. Most of the elements evaluated were efficiently reduced, except for calcium, whose removal rate was comparatively poor, about 54%. The silica removal as determined by gravimetric technique showed low removal (28%). However, the EDAX method showed an 83% reduction.

The hammered-washed and DPTA-treated OPEFB strand was further treated with alkali peroxide by compression-decompression impregnation using a liquor-to-OPEFB ratio of 10. The chemical composition of the treatment liquor was similar to that used by Law et al. (1994). The treated OPEFB strand was heated at 70 °C for 60 min. The resulting surface of the strand was free of silica-bodies, exposing the craters (Fig. 5).

Table 5. Effect of Hammering-washing and DPTA Treatment on Mineral Content

Mineral	Amount in Treated OPEFB	Change*, %	
		Raw	Corrected**
Metals by AAS:			
Iron	0.5 g/g	-	- 94.5
Manganese	0.4 ± 0.0 g/g	- 95.0	- 95.0
Calcium	1.4 ± 0.1 g/g	- 49.3	- 54.1
Copper	0 g/g	- 100	- 100
Sodium	0.8 ± 0.6 g/g	- 93.3	- 93.6
Silica (TAPPI gravimetry)	0.7 ± 0.1 g/g	- 14.1	- 28.6
Silica (EDAX)	0.4 % (atomic)	- 79.6	- 83.3
Yield	92 %		

* Relative to untreated OPEFB
** Corrected for yield

Morphology of OPEFB Ash

Burning of OPEFB strand yielded fascinating feature of the residue. The ash was in close resemblance to fiber, in shape and length. This might indicate a high affinity of lignin towards metals and thus, the shape of the ash of lignin coated fiber. The observation might also explain the association of metals with cellulose as claimed by Mirshokraie and Abdulkhani (2004).
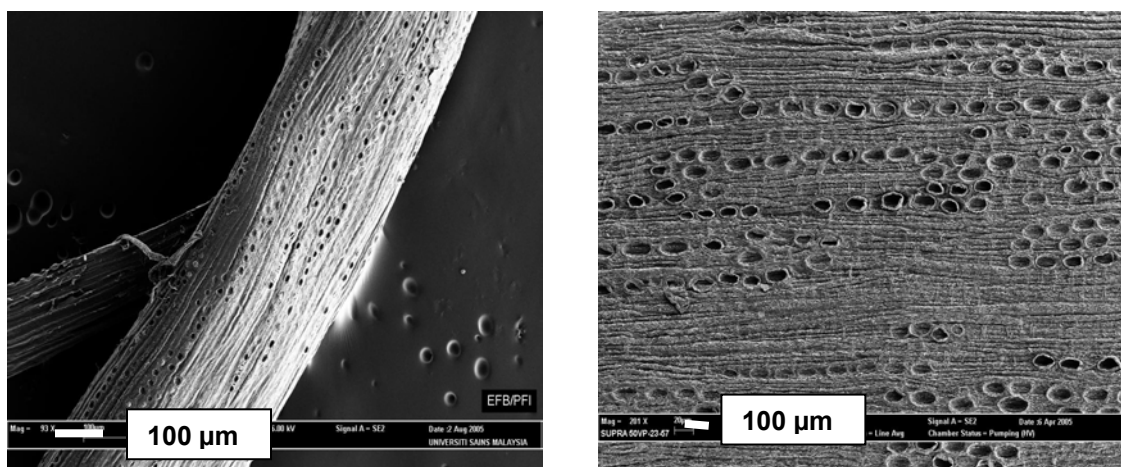
Fig. 5. Surface characteristics after alkali peroxide treatment.

Figure 6 (left, top) represents the ash of untreated natural OPEFB strand. Amazingly, the residue appeared as a perfect reflection of the original fibrous strand. In addition to the fiber-like residue of minerals one can observe the spherical-shaped silica-bodies. The right-top SEM micrograph shows the residue of a handsheet prepared from fibers produced in a simulated alkali-peroxide pulping process. On this micrograph one can easily identify several large vessel elements. A close-up view of the pitted-structure is shown in the left-bottom micrograph. One might also encounter a massive layer of silica-bodies atop a layer of minerals, as shown in the right-bottom micrograph.

The principal elements of a mixed ash residue determined by EDAX are listed in Table 6, which shows that the main components are carbon and oxygen.

Table 6. Elements in mixed ash of OPEFB

Elements	Atomic %
Carbon	46.5
Oxygen	45.2
Magnesium	1.3
Silica	5.5
Sulfur	-
Calcium	0.7
Potassium	-
Copper	0.3

Organization of Minerals and Silica in OPEFB Strand

Setting aside the morphological aspects of an OPEFB strand, and based on the observed physical and chemical characteristics, a hypothesized scheme of the organization of silica-bodies and other minerals is depicted in Fig. 7. Our hypothesis suggests that there exists a network of siliceous pathways within the fibrous strand matrix and that during the growth season basic silica element is transported through this pathway and deposed onto the craters on the surface of the strand. The hypothesis also implies that minerals are distributed along the pathway and concentrated adjacent to the silica-bodies.
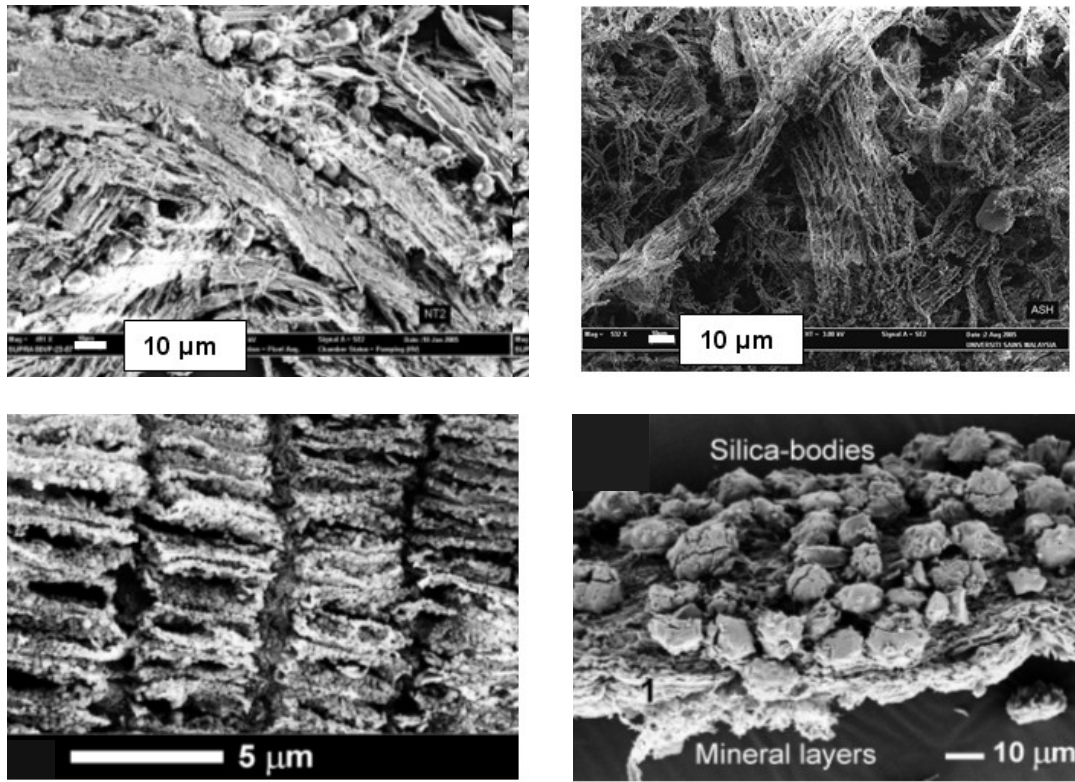
Fig. 6. Fiber-like ash residue of untreated OPEFB (left, top) and handsheet made from alkali peroxide treated fibers (right, top). Ash resembling pit structure of DPTA treated vessel (left, bottom). Silica-bodies encountered atop mineral layer (right, bottom).
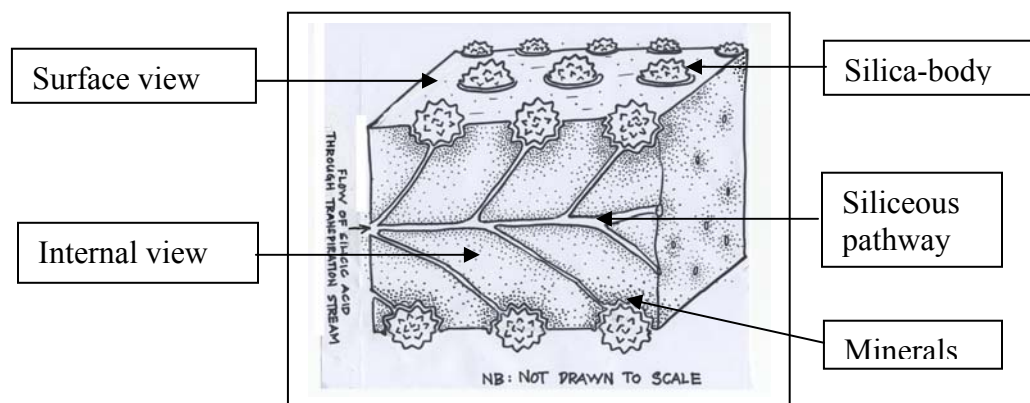

Fig. 7. Hypothesized organization of minerals and silica-body in the matrix of an OPEFB strand: Minerals are indicated by dots.

CONCLUSIONS

1. The vascular strand of OPEFB is unique in structure; it has several large-diametered and long vessel elements in its core region surrounded by vascular fibers.
2. It has large number silica-bodies attached to craters on its surface; the craters have perforated bottoms.
3. The silica-bodies are hard but can be dislodged mechanically from their craters.
4. Large amounts of the minerals including silica can be removed by combined actions of hammering, washing, and DPTA treatment.
5. The principal elements of mixed ash residue determined by EDAX are carbon and oxygen.

ACKNOWLEDGEMENTS

REFERENCES CITED

Berzins, V. (1966). Chemical Composition of woods. Research Note No. 61, Pulp and Paper Research Institute of Canada.

He, Z., Ni, Y. and Zhang, E. (2003). "Comparison of oxalate formation from spruce TMP: Conventional peroxide bleaching process versus the P_M Process," *J. Pulp Paper Scie*. 29(12), 391-394.

Heillila, M. and Vuorinen, T. (2000). "Decomposition of hydrogen peroxide in catalytic cycle," *Proc. Intern. Pulp Bleach. Conf.,* Halifax, NS, Canada, 155-160.

Husin, M., Hassan, A. H. and Ahmad, A. T. (1986). "Availability and potential utilisation of oil palm trunk and oil palm fronds up to year 2000," *Palm Oil Research Institute Malaysia, Report Paper* No. 20.

Jalil, A. A., Kasin, J. and Ramli, R. (1991). *Proc. Natl. Seminar on Oil Palm Trunk and other Palmwood Utilisation*, Kuala Lumpur, Malaysia, FRIM, 12-18.

Khozirah, S., and Khoo, K. C. (1991). "Oil palm stem utilisation – Review of research," in: *Research Pamphlet* No. 107-1991 (S. Khozirah, K. C. Khoo and R. M. A. Abdul, (eds.), School of Industrial Technology, Universiti Sains Malaysia, p. 1-9.

Khoo, K. C., Killmann, W., Lim, S. C. and Mansor. (1991). "Charactersitcs of the oil palm stem," *Research Pamphlet No. 107: Oil Palm Stem Utilisation*, Kuala Lumpur, Malasyia, FRIM, 19-48.

Khoo, K. C. and Lee, T. W. (1991). "Pulp and paper from the oil palm," *Appita J.* 44 (6), 385-388.

Kulkarni, A. G., Mathur, R. M. and Dixit, A. K. (2005). "Desilication of wheat straw black liquor," *Proc. 59th Appita Annual Conference and Exhibition*, Auckland, New Zealand, 16-19 May 2005, Vol. 2, 615-621.

Law, K. N., Luo, S. G. and Valade, J. L. (1994). "Microwave-assisted alkaline peroxide mechanical pulping of aspen," *Cell. Chem. Techn.* 28, 71-83.

Law, K. N. and Jiang, X. (2001). "Comparative papermaking properties of oil-palm empty fruit bunch," *Tappi J.* 84(1), 1-13.

Lins, U., Barros, C.F., Da Cunha, M. and Miguens, F.C. (2002). "Structure, morphology, and composition of silicon biocomposites in the palm tree *Syagrus coronata* (Mart.) Becc.," *Protoplasma* 220, 89-96.

Mansor, H. and Ahmad, A. R. (1991). "Chemical composition of the palm trunk," *Proc. Natl. Seminar on Oil Palm Trunk and other Palmwood Utilisation*, Kuala Lumpur, Malaysia, FRIM, 335-342.

Mirshokraie, S. A. and Abdulkhani, A. (2004). "The effects of water quality on the optical properties of chemimechanical pulp of Northern Iranian hardwood," *Preprints PAPTAC 90th Ann. Meet.,* Book B:B155-B160.

Neumann, D., and De Figueiredo, C. (2002). "A novel mechanism of silicon uptake," *Protoplasma* 220, 59-67.

Pan, X.-J. and Learly, G. J. (2000). "Alkaline peroxide mechanical pulping of wheat straw. Part 2. Stabilization to the peroxide brightening of wheat straw," *Tappi J.* 83(7), 63-66.

Prasakis, J. M., Sain, M. and Daneault, C. (1996). "Metal management improves peroxide bleaching of TMP," Tappi J. 76(10), 161-166.

Richmond, K. E. and Sussman, M. (2003). "Got silicon? The non-essential beneficial plant nutrient," Current Opinion in *Plant Biology* 6 (3), 268-272.

Tanaka, R. and Yamamoto, K. (2004). "Accumulation and availability of oil palm biomass in Malaysia," *In*: Tanaka, R. and Cheng, L.H. (ed.) *Proc. 3rd USM-JIRCAS Joint International Symposium* (9-11 March 2004), Penang, Malaysia, JIRCAS Working Report No. 39, 20-34.

Tutus, A. and Eroglu, H. (2003). "A practical solution to the silica problem in straw pulping," *Appita J.* 56(2), 111-115.

Wan Zahari, M., Sato, J., Furuich, S., and Mohd Sukri, I. (2004). "Recent development on the processing and utilisation of complete feed based on oil palm fronds for ruminant feeding in Malalysia," *In*: Tanaka, R. and Cheng, L.H. (ed.) *Proc. 3rd USM-JIRCAS Joint International Symposium* (9-11 March 2004), Penang, Malaysia, JIRCAS Working Report No. 39, 24-27.

Zhao, X., Odberg, L. and Risinger, G. (1992). "Beating of wheat-straw pulp: Dissolved carbohydrates and lignins, fibre swelling and fines generation," *Tappi J.* 75(1), 153-161.