# Characteristics of Pulp Fibers as Green Potential Polymer Reinforcing Agents

Nanang Masruchin, Subyakto

Laboratorium Biokomposit, UPT Balai Litbang Biomaterial, Lembaga Ilmu Pengetahuan Indonesia (LIPI) Jl. Raya Bogor KM 46 Cibinong Bogor

*Corresponding author*: masruchin@biomaterial.lipi.go.id (Nanang Masruchin)

**Abstract**

Three kinds of pulps (i.e kenaf, pineapple and coconut fiber) were characterized as reinforcing agents in composite materials to be applied at automotive interior industry. A better understanding on characteristics of fiber will lead to enhance interface adhesion between fiber and matrices. Chemical, surface compositions, and morphology of pulp fiber were investigated using TAPPI standard test method, Fourier Transform Infrared Spectroscopy and optical microscopy, respectively. Morphology of fiber was investigated by Scanning Electron Microscopy. Pineapple pulps showed the highest α-cellulose content than that of kenaf or coconut pulps. However, it has the lowest hemicellulose content among them. This condition takes responsibility for the difficulties of pineapple pulps defibrillation process. Much fines or external fibrillations are presence on both kenaf and pineapple pulp's morphology, but it is not presence in the coconut pulps. Coconut fiber is shorter than the other two fibers with diameter size estimated in the order pineapple < kenaf < coconut pulps. FTIR analysis shown quite similar absorption from all pulps, except for coconut pulps due to the remaining lignin on the surface of fiber that showed by the presence of C-O phenol stretching at 1280 $cm^{-1}$. Kenaf pulps fiber is suitable candidate for polymer reinforcing agents compared to pineapple and coconut pulps fiber.

**Key words*:*** cellulose, characteristics, composite, interface, pulp fibers

## Introduction

Recently, global warming concern and environmental awareness force the manufacturing of green or eco-friendly technology. European Union legislation implemented in 2006 has expedited recent natural-fiber-reinforced plastic automotive insertion; by 2006, 80% of a vehicle must be reused or recycled and by 2015 it must be 85%. Japan requires 88% of a vehicle to be recovered (which includes incineration of some components) by 2005, rising to 95% by 2015. As a result, today most automakers are evaluating the environmental impact of a vehicle's entire lifecycle, from raw materials to manufacturing to disposal (Holbery & Houston 2006). Consideration of lightweight material, low cost natural fibers offers the potential to replace a large segment of the glass and mineral fillers in numerous automotive interior and exterior parts. Moreover, by replacing the fillers with the renewable fibers, not only reduce the mass of the component but also lower the energy needed for production by 80% (Malkapuram *et al.* 2009). In addition, reduction in weight of car means reduce gas emission to surrounding.

Introducing natural fibers into polymer composites has several drawbacks due to incompatibility with the hydrophobic polymer matrix, the tendency to form aggregates during processing, poor

resistance to moisture and low thermal stability are greatly reduce the potential of natural fibers to be used as reinforcement in polymers (Saheb & Jog 1999). Therefore, understanding the interface between matrix and filler is importance, as well as morphology, chemical composition, surface energy, thermal stability of the fibers will lead to better enhance adhesion resulting in improvement in strength and impact properties (Jacob *et al.* 2005, Bledzki *et al.* 2006, John & Thomas 2008). Saputra *et al.* (2004) studied the effect of extractives in wood flour on the mechanical properties of wood-polypropylene (PP) composites. A large increase in the strength of pine flour-PP composites was observed upon removal of extractives from pine flour, however there was no changes detectable in the percent crystallinity and the formation of spherulite size or shape of PP composites. Effect of lignin on the heat and light resistance of lignocellulosic fibers was studied by Reddy *et al.* (2007). It is reported that existence of lignin in lignocellulosic fibers increases the loss in breaking tenacity and elongation of kenaf fibers when they are exposed to heat and light. Therefore, the delignified fibers have higher resistance to heat and light exposure compared to the untreated fibers. In addition, the influence of hemicelullose content as a part of major component in lignocellulosic material is attracting study in the utilization of natural fibers (Gumuskaya *et al.* 2007, Iwamoto *et al.* 2008).

The objective of this study is to elaborate the morphology, chemical composition of three non-wood fibers as polymer reinforcing agents.

## Materials and Methods

Three kinds of non-wood fiber were subjected in this study. Coconut fibers and pineapple fibers were collected from local industry in Sukabumi and Subang, respectively. While, kenaf bast fibers was collected from PT. Abadi Barindo Autotech (ABA), Pasuruan. A lot of varies in size, quality and species were limited to the utilization of natural fibers into polymer composites due to resulting in different mechanical properties (John & Thomas 2008). Therefore, all fibers were obtained as received and processed into pulp fibers to obtain homogenous size (diameter and shape) among the fibers. Converted bulk fibers into pulp fibers also resulted in a flexible fibers due to the plastic deformations during mechanical refining process (Hamad 1997), higher mechanical properties (Page *et al*. 1971), and also higher thermal stability due to the removal of non-cellulosic compound (Mothe & Miranda 2009), which were all filler requirement for reinforcing agents in polymer composites.

### Pulping process

Methods, cooking conditions and temperature for pulping process were shown in Table 1. Dried fibers were cut into 3-5 cm long. Kenaf and pineapple fibers were processed using soda process, while coconut fibers were processed in kraft pulping method. This method was chosen to obtain higher yield of pulping process and due to the higher lignin content especially for coconut fibers (John & Thomas 2008). After pulping process, the fibers were fibrillated using disc refiner in 8 cycles for each pulp. Pulps then filtered and formed it into sheet and then dried in an oven at 75$^{o}$C for three days. Dried pulps were subjected for further characterization.

**Determination of chemical composition of pulps**

Chemical compositions of three pulp samples were determined using TAPPI test standart. In Table 2, it is presented kind of carbohydrate component contents and the standard methods that we used.

**FTIR analysis**

The powder of pulp samples obtained was used for FTIR spectroscopy measurements. The dried pulp samples were embedded in KBr pellets, and were analyzed by using a Bruker Tensor 37. They were recorded in the absorption mode in the range 4000–400 $cm^{-1}$ with an accumulation of 32 scans, resolution of 4 $cm^{-1}$.

**Morphology structure analysis**

Morphology of pulp samples were characterized using Optical Microscopy NIKON Eclipse 80i. Pulp's diameter was determined from captured picture obtained from optical microscopy using software Motic Images Plus 2.0. Further analysis on morphology with high magnification was performed by SEM JEOL JSM 5310 LV. Pulp samples was mounted on stub and coating with gold using a sputter canter and then scanning was running at 20kV voltage.

**Result and Discussion**

**Chemical composition of pulps**

The plant cell wall is composed of cellulose, lignin, hemicelluloses, and extractives. Thus, the surface energy of the plant material must be some combination of the surface energies (γ) of these components (Liu & Rials 1998). The surface energy of fibers takes a lot responsible for the adhesion mechanism between reinforcing agents and polymer (Heng *et al.* 2007). Therefore, quantitative amount of these components especially in the surface of fibers will influence the properties of the fiber in composites.

Table 1 Conditions of pulping processes

| Fiber | Methods | Cooking conditions | Temperature |
|---|---|---|---|
| Coconut | Kraft | Active alkali, 18%<br>Sulfidity 30%<br>Liquor:raw material = 4:1 | 1,5 hours to reach 165$^{o}$C, then was kept at 165$^{o}$C for 2,5 hours |
| Kenaf | Soda | Active alkali, 17%<br>Liquor:raw material = 4:1 | 1,5 hours to reach 170$^{o}$C, then was kept at 170$^{o}$C for 1,5 hours |
| Pineapple | Soda | Active alkali, 10%<br>Liquor:raw material = 4:1 | 2 hours to reach 160$^{o}$C, then was kept at 160$^{o}$C for 1,5 hours |

Table 2 Chemical components standard testing methods

| Carbohydrates components | Standard methods |
|---|---|
| Extractives | TAPPI TM T204 OS76 |
| Klason lignin | TAPPI TM T222 OM88 |
| Hemicellulose | TAPPI TM T223M |
| α-Cellulose | TAPPI TM T203 OM88 |

Extractives content of three pulps were approximately 0.5 - 1.2% (Figure 1a). Compare to the others component, the amount of extractive is quite low. Alkali solution during pulping process removes extractives from the fibers as well as the use of high pressure and temperature of pulping. Plant extractives are hydrophobic substances with low molecular weights. Since most thermoplastics polymer are processed at high temperatures, around 170-190 $^{o}$C, (i.e. mixing, injection molding, extrusion), the thermal stability of the fibers at processing temperatures is important. At such high temperatures, plant extractives may tend to migrate to the fibers surface, and accumulate in the interface layer and decrease the adhesion mechanism (Saputra *et al.* 2004). Kenaf pulps has the lowest extractives content compare to the other pulps. Liu and Rials (1998) explained that removing most extractives from the wood fiber, might increase dispersive component of the surface energy ($\gamma_d$), increased the acidity, and increased the basicity, whereas, acidity and basicity will take responsible in the adhesion mechanism between fiber and polymer (Heng *et al.* 2007, Hull 1971). Moreover, water soluble extractives could have a significant effect on the wettability, strength, modulus, shrinkage and durability of the fiber (Shebani *et al.* 2008).

Lignin content of pulps are presented in Figure 1b. Coconut pulps has the highest lignin content compared to the other pulps, as well as expected, which indicated that lignin still remain on the surface of coconut pulps. Reddy *et al.* (2007) explained that the existence of lignin in lignocellulosic fibers increases the loss in strength and elongation of fibers when they are exposed to heat and light. Which is fiber with high strength and elongation may be useful in the context of a composite material, particularly for enhancing toughness of a natural fiber

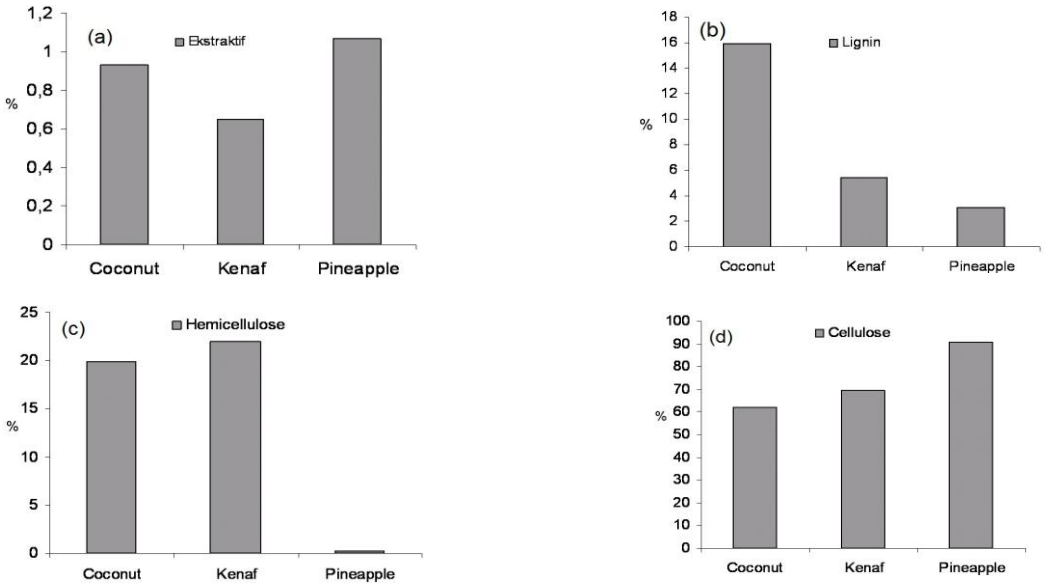


Figure 1 Chemical compositions (%) of three pulp fibers. (a) Extractives, (b) Lignin, (c) Hemicellulose and (d) Cellulose.

based material (Bakri & Eichhorn 2010). The lignin content will influence the thermal stability of the fibers. Therefore, a coconut fiber which has the highest lignin content may lead to the lowest thermal stability during processing in high temperature.

Hemicellulose was the second major component of pulps fiber. Interestingly, the percentage of hemicellulose of pineapple pulps fiber was the lowest content, which is only 0.24% (Figure 1c). During the mechanical fibrillation, it was very difficult to defibrillate the pineapple pulps. Although in this research, we did not measure the energy require for defibrillation process, it could be noted that the energy needed to process pineapple was higher than the other two pulps. It is reported that the hemicellulose most responsible for the swelling or increase in the plasticity of cellulose. Since pineapple pulp fibers had low hemicellulose contents, this situation could affect swelling, defibrillation and beating of pulp obtained from pineapple fibers (Gumuskaya *et al*. 2007). In addition, it is noted that compared with the fibers of extremely low hemicellulose content, an increase in hemicellulose content leads to increased pulp fiber strength. It suggests that this is due to improved stress transfer between cellulose crystallites in the presence of amorphous hemicellulose (Henriksson *et al*. 2008). According to research of Iwamoto *et al.* (2008), they produced nanocellulose from wood pulp, the presence of hemicelluloses reported could act as inhibitors of the coalescence of microfibrils during drying and facilitate the nanofibrillation of once-dried pulps. Therefore, high hemicellulose content was desired for easy handling of fibrillation process during preparation of fibers as reinforcing polymer. Kenaf pulps show the highest hemicellulose content (Figure 1c).

Cellulose was the major component of pulp fibers. From Figure 1d, it is shown that cellulose content of pineapple pulp fibers was the highest. The mechanical properties of fiber are dependent on the cellulose content, degree of polymerization, and microfibrillar angle (MFA). Fibers with higher cellulose content, higher degree of polymerization and a lower microfibrillar angle exhibit higher tensile strength and modulus (Jacob *et al.* 2005). During processing of composites, pulp fibers were formed into dried-sheet. It will be added into melt polymer and mixed to obtain highly degree of dispersion filler in the matrix. Due to high cellulose content and very low hemicellulose content, pineapple pulp fibers sheet was very difficult to disperse in matrix. It caused by the very strong hydrogen bonding that caused agglomeration of pulp fibers (Iwamoto *et al.* 2008). From the chemical component analysis, kenaf pulp fibers have higher cellulose and hemicellulose content; however, it has the lower lignin and extractives content. Therefore, it is suitable to be applied as reinforcing in polymer composites.

### *Infra-red spectra*

The IR spectra show the composition of the pulp samples, the absorption spectrum on the infrared region of the three pulp samples can be observed in the Figure 2 and Table 3. The main characteristics are attributed to the presence of lignin, hemicellulose and cellulose. In general, the IR spectra for the native and the chemically modified fibers are representative in the 3,000–3,600 $cm^{-1}$ range. The large band is attributed to the axial deformation of the O–H group. At 3,000–2800 $cm^{-1}$ band is related to the

axial deformation of C–H group, while the one at 1,630 $cm^{-1}$ is related to the C=C stretching vibrations (Tserki *et al*. 2005a). The methoxyl group gives signal at 1,430 $cm^{-1}$, while the band at 1,058 $cm^{-1}$ is associated to the presence of C–O–C in cellulose chain. The absorption spectrum for three pulp samples presents some structural similarities, except for the coconut pulps. Absorption at band 1280 $cm^{-1}$ that only present in coconut pulp samples is representative of C-O phenol stretching, which is the lignin constituent still remain on the surface of fibers after pulping process (see Table 3). Some of reactive functional group (hydroxyl, carboxyl) of lignocellulosic fiber is sensitive to chemical treatment, such as esterification, acetylation, propionylation and another functionalization. These treatments are needed to improve thermal, mechanical and compatibility of fiber during filler reinforcement in polymer. The highest extent of the esterification reaction was achieved for the plant fibers due to their high lignin or hemicelluloses content in the fibers (Tserki *et al*. 2005b). Therefore, it is necessary to obtain lot of reactive group for chemical treatment on the surface of fibers.

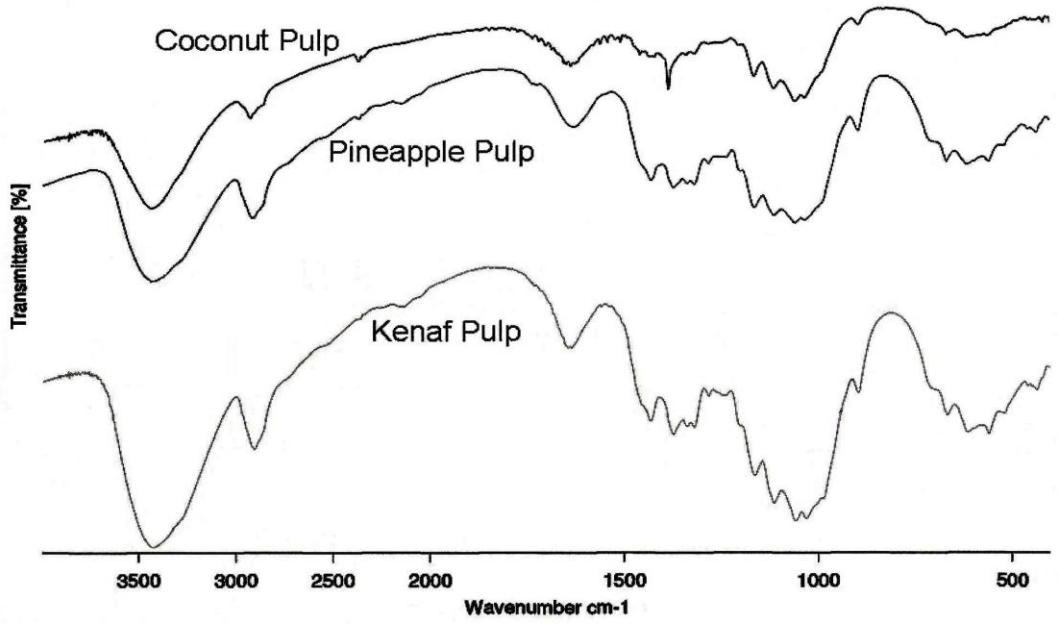


Figure 2 Infra-red spectra of three pulps fiber.

Table 3 Functional groups of infra-red spectroscopy of three pulps fiber

| Wave number ($cm^{-1}$) (Yang *et al.* 2007) | Coconut Pulp | Kenaf Pulp | Pineapple Pulp | Functional groups | Compounds |
|---|---|---|---|---|---|
| 3600 – 3000 | 3428 | 3415 | 3402 | OH-stretching | Acid, methanol |
| 2860 – 2970 | 2920 | 2901 | 2904 | $C\text{-}H_n$ stretching | Aliphatic |
| 1700 – 1730, 1510 – 1560 | 1560 | - | - | C=O stretching | Ketone and carbonyl |
| 1632 | 1635 | 1643 | 1629 | C=C | Benzene stretching range |
| 1470 – 1430 | 1425 | 1431 | 1429 | $O\text{-}CH_3$ | Methoxyl-O-$CH_3$ |
| 1215 | 1280 | - | - | C-O stretching | Phenol |
| 1170, 1082 | 1164, 1058 | 1058 | 1059 | C-O-C stretching | Pyranose ring skeletal |
| 700-900 | 896 | 896 | 897 | C-H | Aromatic hydrogen |

***Morphology structure***

Morphology study of three pulp fibers was analyzed using optical and scanning electron microscopy (Figure 3 and 4). Coconut pulp fibers have diameter ranging from 20 to 27 μm, kenaf pulps have diameter ranging from 10 to 20 μm and pineapple pulp fibers have the lowest diameter ranging from 3 to 7 μm. From images analyze, it shown that coconut pulp fibers have short length compared to the other two pulps (Figure 3a). Kenaf pulps shown to fracture/break due to mechanical refining which fatigue loading involve to the fibers (see Figure 3b). Much fines and external fibrillation occur on the surface of kenaf and pineapple pulps. However, it did not occur in the case of coconut pulps. These finding using optical microscopy was supported with the images resulted from SEM (Figure 4a, b and c).

The differences of morphology, size, shape and surface roughness of fibers will influence the formation adhesion between filler and matrix polymer. The mechanical characteristics of a fiber-reinforced composite depend not only on the properties of the fiber, but also on the degree to which an applied load is transmitted to the fibers by the matrix phase.

.

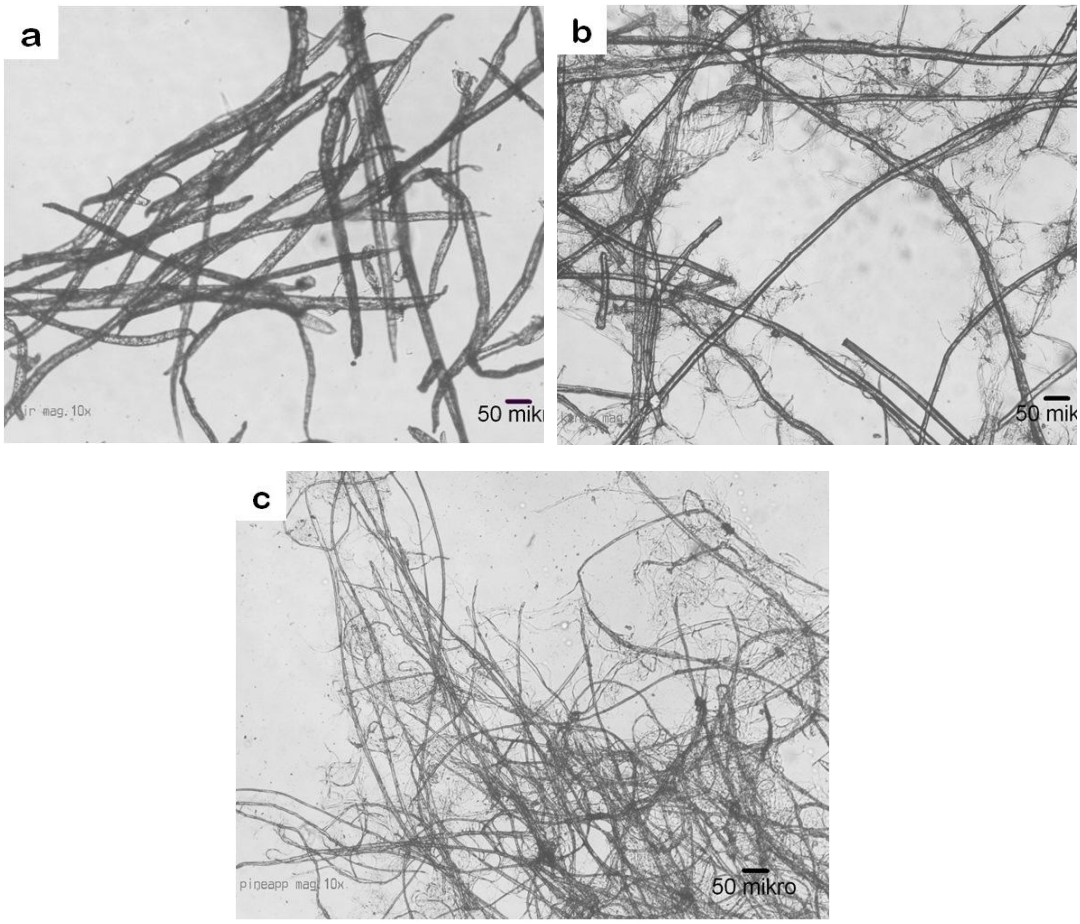


Figure 3 Optical microscopy images of three pulps fiber at 10 times magnification. (a) Coconut (b) Kenaf and (c) Pineapple pulps.

Some critical fiber length ($l_c$) is necessary for effective strengthening and stiffening of the composite material. Critical fiber length—dependence on fiber strength and diameter, and fiber-matrix bond strength/matrix shear yield strength ($\tau_c$) (Callister 2007). As fiber length ($l$) increases, the fiber reinforcement becomes more effective ($l > l_c$), as well as the increase of aspect ratio (l/d) of the fibers. Therefore, pineapple and kenaf fibers showed higher in aspect ratio. According to Lenes *et al.* (2006), it is clearly show that a Polypropylene (PP) composite with fibrillated cellulose fibers (much fines) were induce a high degree of transcrystallization of PP. Therefore, fibrillated pulp will be desired since it acts as nucleating sites of thermoplastic polymer during crystallization.

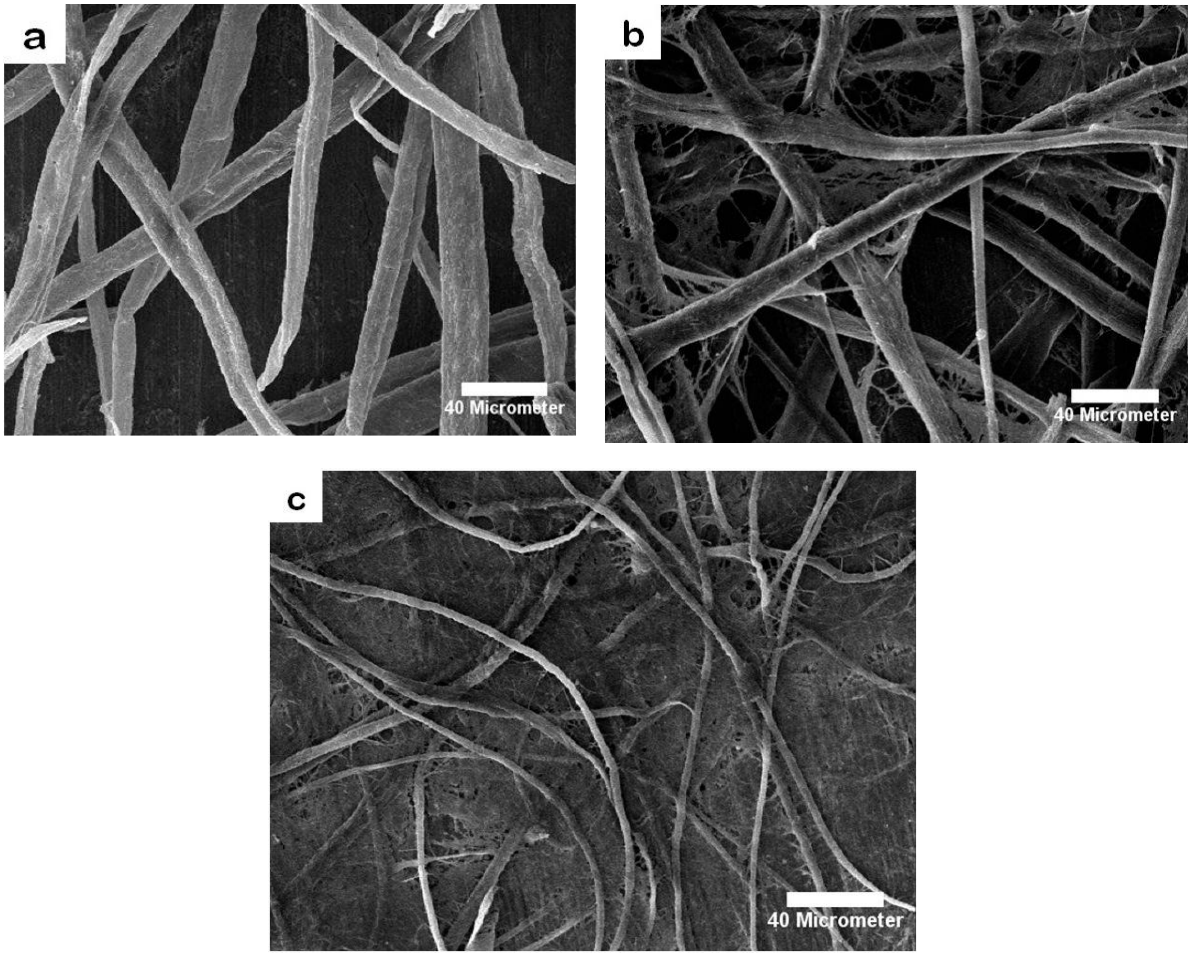


Figure 4 SEM images of three pulps fiber, (a) Coconut (b) Kenaf and (c) Pineapple pulps.

## Conclusion

Pulping process of three non-wood fibers was conducted to obtain homogeneous dimension and large surface area of fibers. These fibers were characterized as polymer reinforcing agents. From this study, pineapple pulps have the lowest hemicellulose content which is responsible to the difficulties of fibrillation process. FTIR study supported that coconut pulps have the highest lignin content, which kenaf pulps have the moderate chemical constituents. Optical and SEM analysis shown that both kenaf and pineapple pulps were fibrillated. However, it did not occur on the surface of coconut pulps. The diameter of pulps ranging from 3 to 30 μm which coconut pulps fiber has the highest diameter and the shortest in length. It can be concluded that kenaf pulps fiber were the best candidate for polymer reinforcing agents, taking easier processing (fibrillation) of pulps fiber as consideration in spite of pineapple fibers. Furthermore, it should be pointed out that surface energy, chemical composition, crystal morphology and moisture content are of importance to the nucleation of thermoplastic polymer.

## Acknowledgements

The author wish to thank to Mr. Wawan Kartiwa Haroen, Researcher at Balai Besar Pulp dan Kertas, Bandung; Lucky Risanto, S.Si; Widya Fatriasari, S.Hut, MM and

Teguh Darmawan, ST for kindly discussion and help.

## References

Bakri B, Eichhorn SJ. 2010. Elastic coils: deformation micromechanics of coir and celery fibres. *Cellulose* 17: 1-11.

Bledzki AK, Faruk O, Sperber VE. 2006. Cars from Bio-Fibres. *Macromol. Materials Eng.*291: 449–457.

Callister WD. 2007. *Materials Science and Engineering, An Introduction*, the 7th ed. USA: John Wiley & Sons Inc.

Gumuskaya E, Usta M, Balaban M. 2007. Carbohydrate components and crystalline structure of organosolv hemp (*Cannabis sativa* L.) bast fibers pulp. *Biores Technol* 98: 491–497.

Hamad WY.1997. Some microrheological aspects of wood pulp fibres subjected to fatigue loading. *Cellulose* 4: 51-56.

Heng JYY, Pearse DF, Thielmann F, Lampke T, Bismarck A. 2007. Methods to determine surface energies of natural fibres: a review. *Composite Interfaces* 14: 581–604.

Henriksson M, Berglund LA, Isaksson P, Lindstrom T, Nishino T. 2008. Cellulose Nanopaper structures of high toughness. *Biomacromolecules* 9: 1579–1585.

Holbery J, Houston D. 2006. Natural-fiber-reinforced polymer composites in automotive applications. *J Minerals, Metals Materials Soc* 58(11): 80-86

Hull D. 1981. An introduction to composite materials, *In: Fibre-matrix interface*. Cambridge: Cambridge University Press. Pp. 36-42.

Iwamoto S, Abe K, Yano H. 2008. The effect of hemicelluloses on wood pulp nanofibrillation and nanofiber network characteristics. *Biomacromol.* 9: 1022–1026.

Jacob M, Joseph S, Pothan LA, Thomas S. 2005. A study of advances in characterization of interfaces and fiber surfaces in lignocellulosic fiber-reinforced composites. *Composite Interfaces* 12(1-2): 95–124.

John MJ, Thomas S. 2008. Biofibres and biocomposites, *Carbohydrate Poly*. 71: 343–364.

Lenes M, Gregersen WO. 2006. Effect of surface chemistry and topography of sulphite fibres on the transcrystallinity of polypropylene. *Cellulose* 13: 345–355.

Liu FP, Rials TG. 1998. Relationship of wood surface energy to surface composition. *Langmuir* 14: 536-541.

Malkapuram R, Kumar V, Negi YS. 2009. Recent development in natural fiber reinforced polypropylene composites. *J Reinforced Plastics Composites* 28: 1169-1189.

Mothe CG, de Miranda IC. 2009. Characterization of sugarcane and coconut fibers by thermal analysis and FTIR, *J Thermal Analysis Calorimetry* 97: 661-665.

Page DH, El-Hosseiny F, Winkler K. 1971. Behaviour of single wood fibers under axial tensile strain. *Nature* 229: 252-253.

Reddy N, Salam A, Yang Y. 2007. Effect of lignin on the heat and light resistance of lignocellulosic fibers. *Macromolecular Materials Engineering* 292:458–466.

Saheb DN, Jog JP. 1999. natural fiber polymer composites: a review. *Advances Poly Technol* 18: 351–363.

Saputra H, Simonsen J, Li K. 2004. Effect of extractives on the flexural properties of wood/plastic composites. *Composite Interfaces* 11(7):515–524.

Shebani AN, van Reenen AJ, Meincken M.2008. The effect of wood extractives on the thermal stability of different wood species. *Thermochimica Acta* 471:43-50.

Tserki V, Matzinosa P, Kokkoub S, Panayiotou C. 2005a. Novel biodegradable composites based on treated lignocellulosic waste flour as filler. Part I. Surface chemical modification and characterization of waste flour. *Composites: Part A* 36: 965-974.

Tserki V, Zafeiropoulos NE, Simon F, Panayiotou C. 2005b. A study of the effect of acetylation and propionylation surface treatments on natural fibres. *Composites: Part A* 36: 1110–1118.

Yang H, Yan R, Chen H, Lee DH, Zheng C. 2007. Characteristics of hemicellulose, cellulose and lignin pyrolysis. *Fuel* 86: 1781–1788.

Riwayat naskah (*article history*)

Naskah masuk (*received*): 25 Juli 2011
Diterima (*accepted*): 30 Oktober 2011