

INVESTIGATION CHARACTERISTICS OF PULP FIBERS AS GREEN POTENTIAL POLYMER REINFORCING AGENTS

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ABSTRACT

INVESTIGATION CHARACTERISTICS OF PULP FIBERS AS GREEN POTENTIAL POLYMER REINFORCING AGENTS. Three kinds of pulp fiber (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. Furthermore, it will improve the properties of polymer significantly. Chemical, surface compositions as well as morphology of pulp fiber were investigated using TAPPI standard test method, Fourier Transform Infrared Spectroscopy (FT-IR) and optical microscopy, respectively. Further observation on morphology of the fiber was conducted by Scanning Electron Microscope (SEM). From this study, 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. Moreover, coconut fiber is shorter than the other two fibers with diameter size estimated in the order pineapple < kenaf < coconut pulps. FT-IR 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} . Finally, it is reported that kenaf pulps fiber is suitable candidate for polymer reinforcing agents compared to pineapple and coconut pulps fiber.

Keywords: Pulp fibers, Cellulose, Characteristics, Interface, Composite

ABSTRAK

INVESTIGASI KARAKTERISTIK SERAT PULP NON KAYU SEBAGAI PENGUAT PADA KOMPOSIT POLIMER. Tiga jenis serat pulp dihasilkan dari proses *pulping* (kraft dan soda) dari serat alam non-kayu yaitu serat kenaf, nanas dan sabut kelapa. Serat tersebut akan dijadikan sebagai penguat dalam material biokomposit untuk komponen interior dalam industri kendaraan. Pemahaman yang komprehensif pada sifat-sifat serat alam akan memberikan interaksi antara permukaan polimer dan serat alam yang baik sehingga dapat meningkatkan performa kinerja dari komposit yang dihasilkan (sifat mekanis, panas dan kristalisasi polimer). Kandungan kimia serat pulp dianalisa dengan metode *TAPPI test* dan *Fourier Transform Infrared (FT-IR)*, sedangkan struktur morfologi serat dianalisis dengan mikroskop optik dan *Scanning Electron Microscope (SEM)*. Dari penelitian ini diketahui bahwa serat nanas memiliki kandungan selulosa lebih tinggi jika dibandingkan serat kenaf dan kelapa. Namun, memiliki kandungan hemiselulosa paling rendah, dimana hal ini sangat berpengaruh pada proses fibrilasi serat nanas. Pada permukaan serat kenaf dan nanas banyak terbentuk serabut (*fines*) namun tidak demikian dengan pada serat kelapa. Serat kelapa lebih pendek jika dibandingkan dengan dua serat lain, serta dimensi diameter dalam urutan sebagai berikut serat nanas < serat kenaf < serat kelapa. Hasil analisis *FT-IR* menunjukkan serapan yang hampir sama diantara ketiga jenis serat, namun kandungan lignin yang tinggi pada serat kelapa ditunjukkan dengan serapan C-O fenol yang kuat pada 1280 cm^{-1} . Sehingga, dari pembahasan makalah ini dapat disimpulkan bahwa serat kenaf memberikan potensi yang lebih baik untuk dipergunakan sebagai penguat dalam komposit polimer.

Kata kunci: Serat Pulp, Selulosa, Karakteristik, *Interface*, Komposit

INTRODUCTION

Recently, global warming concern and green or eco-friendly technology. European Union environmental awareness force the manufacturing of 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 [1]. 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 % [2]. In addition, reduction in weight 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 [3,4]. Therefore, understanding the interface between matrix and filler is important, 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 [5-7]. The effect of extractives in wood flour on the mechanical properties of wood-polypropylene (PP) composites [8]. 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 reported [9]. 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 hemicellulose content as a part of major component in lignocellulosic material is attracting study in the utilization of natural fibers [10,11].

The objective of this study is to elaborate the morphology, chemical composition of three non wood fibers as polymer reinforcing agents. This study is important because deeply exploring to the potential filler will provide guidance for economically commercialization of natural fiber polymer composites. Coconut, pineapple and kenaf fibers are converted into pulps to obtain higher surface area, better mechanical properties and removing impurities. Chemical compositions of pulps were determined using TAPPI test standart, and briefly FT-IR analysis, whereas, the morphology of pulps were characterized using optical and SEM analysis. It is

reported that kenaf pulps fiber is suitable candidate for polymer reinforcing agents compared to pineapple and coconut pulps fiber.

EXPERIMENTAL 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 [7]. 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 [12], higher mechanical properties [13], and also higher thermal stability due to the removal of non-cellulosic compound [14], 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 [7]. After pulping process, the fibers were

Table 1. Conditions of pulping processes

Fiber	Methods	Cooking conditions	Temperature
Coconut	Kraft	Active alkali, 18% Sulfidity 30% Liquor:raw material = 4:1	1,5 hours to reach 165 °C, then was kept at 165 °C for 2,5 hours
Kenaf	Soda	Active alkali, 17% Liquor:raw material = 4:1	1,5 hours to reach 170 °C, then was kept at 170 °C for 1,5 hours
Pineapple	Soda	Active alkali, 10% Liquor:raw material = 4:1	2 hours to reach 160 °C, then was kept at 160 °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

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 °C for three days. Dried pulps were subjected to next 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.

FT-IR 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.

RESULTS AND DISCUSSION

Chemical Composition of Pulps

Carbohydrate components from each pulp were presented in Figure 1. 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 [15]. The surface energy of fibers takes a lot responsible for the adhesion mechanism between reinforcing agents and polymer [16]. Therefore, quantitative amount of these components especially in the surface of fibers will influence the properties of the fiber in composites.

Extractives component from three pulps approximately between 0.5 - 1.2 %, as can be seen in Figure 1(a). Compare to the others component, it was shown that the amount of extractive is quite low. Alkali solution during pulping process removes this component 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

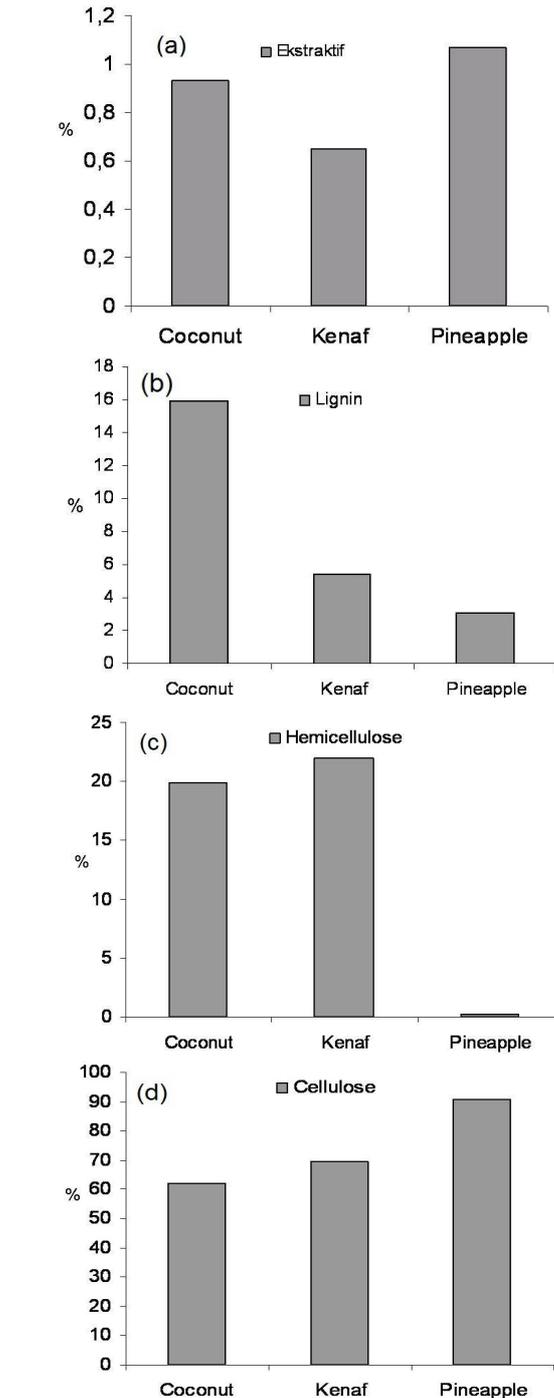


Figure 1. Chemical compositions (%) of three pulp fibers (a). Extractives, (b). Lignin, (c). Hemicellulose and (d). Cellulose

thermoplastics polymer are processed at high temperatures, around 170-190 °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, thus accumulating in the interface layer and decrease the adhesion mechanism [8]. Kenaf pulps show the lowest extractives content compare to the other two pulps. Liu *et al.* [15] explained that

removing most extractives from the wood fiber, resulting in an increased dispersive component of the surface energy (γ_d), increased the acidity, and increased the basicity, whereas, acidity and basicity will take responsible in the adhesion mechanism between fiber and polymer [16,17]. Moreover, it is reported that water soluble extractives could have a significant effect on the wettability, strength, modulus, shrinkage and durability of the fiber [18].

Lignin content of pulp samples are presented in Figure 1(b). It is shown that coconut pulps show the highest lignin content compared to the other two pulps, as well as expected. It is proofed that lignin still remain on the surface of coconut pulps. The existence of lignin in lignocellulosic fibers increases the loss in strength and elongation of fibers when they are exposed to heat and light [9]. 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 based material [19]. Meanwhile, the lignin content will influence the thermal stability of the fibers, i.e. with the highest lignin content, therefore, it is predicted that coconut fibers will lead the lowest thermal stability during processing in high temperature.

Hemicellulose was the second major component of pulps fiber. Interestingly, from Figure 1(c), it can be seen that the percentage of hemicellulose of pineapple pulps fiber was the lowest content, which is only 0.24 %. 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 [11].

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 [20]. Furthermore, producing nanocellulose from wood pulp, hemicelluloses 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. From Figure 1(c), Kenaf pulps show the highest hemicellulose content.

Cellulose was the major component of pulp fibers. From Figure 1(d). It is shown that cellulose content of pineapple pulp fibers was the highest. The mechanical properties of fiber are dependent on the cellulose content

and the degree of polymerization and also microfibrillar angle (MFA). Fibers with higher cellulose content, higher degree of polymerization and a lower microfibrillar angle exhibit higher tensile strength and modulus [5]. 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 [10].

From the chemical component analysis of three pulps samples, it is shown that 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 [21]. 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 (Table 3). Some of reactive functional group (hydroxyl, carboxyl) of lignocellulosic fiber is sensitive to chemical treatment, such as esterification, acetylation,

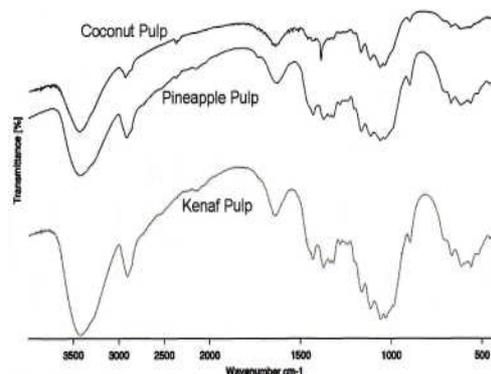


Figure 2. Infra red spectra of three pulp fibers.

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

Wave number (cm ⁻¹) [23]	Coconut Pulp	Kenaf Pulp	Pineapple Pulp	Functional groups	Compounds
3600 – 3000	3428	3415	3402	OH-stretching	Acid, methanol
2860 – 2970	2920	2901	2904	C-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-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

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 [22]. Therefore, it

is necessary to obtain lot of reactive group for chemical treatment on the surface of fibers.

Morphology Structure

Morphology study of three pulp fibers was analyzed using optical and scanning electron microscopy. The images can be seen in Figure 3 and Figure 4, respectively. 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 3(a)).

Kenaf pulps shown to fracture/break due to mechanical refining which fatigue loading involve to the fibers (Figure 3(b)). 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 (Figures 4(a), 4(b) and 4(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. 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 (τ_c)% [24]. 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.

Besides that, according to the study of research [25] it is clearly show that a Polypropylene (PP) composite with fibrillated fibers (much fines) were induce a high degree of transcrystallization of PP.

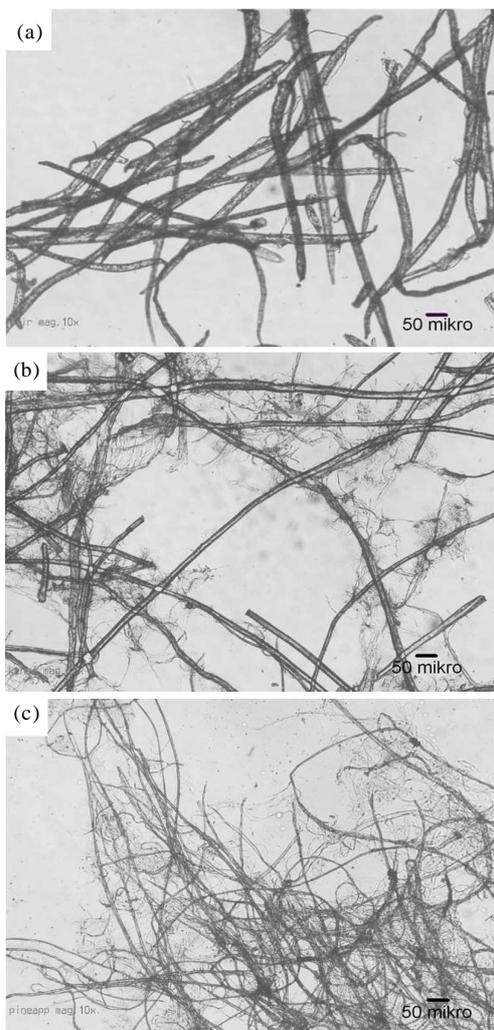


Figure 3. Optical microscopy images of three pulps fiber at 10X magnification (a). Coconut (b). Kenaf and (c). Pineapple pulps.

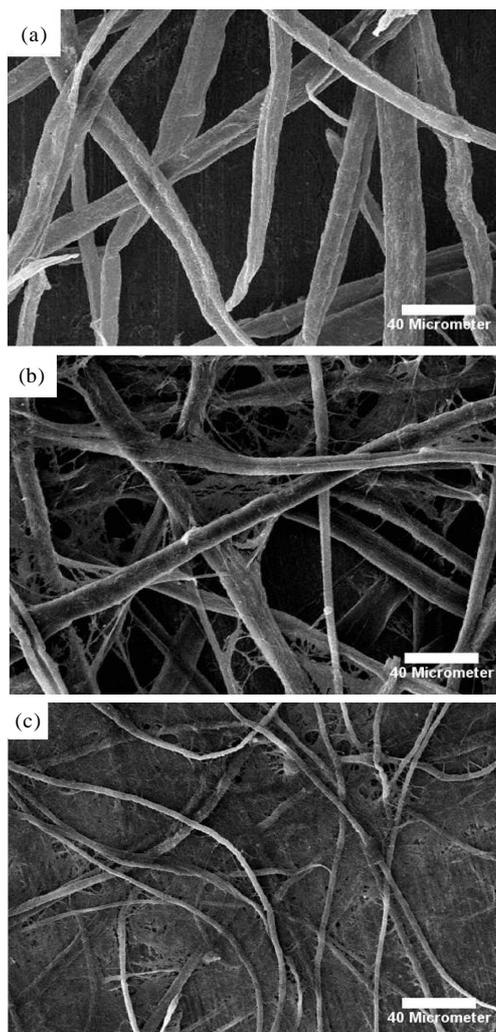


Figure 4. SEM image of three pulps fiber (a). Coconut (b). Kenaf and (c). Pineapple pulps

Therefore, fibrillated pulp will be desired since it acts as nucleating sites of thermoplastic polymer during crystallization.

CONCLUSIONS

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, it is shown that pineapple pulps have the lowest hemicellulose content which is responsible to the difficulties of fibrillation process. FT-IR 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. Therefore, the study of crystal structure of these pulps fiber will be our next topic research to explore the properties of natural fibers as reinforcing agents in polymer.

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