Extraction and characterization of cellulose fiber of durian rinds from north sumatera as the raw material for textile fiber

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Abstract. Cellulose is a kind of biopolymer that abundance in nature. Cellulose has been utilized in the wide area, i.e. textile fibre. Cellulose fibre for this kind of application was obtained from the fibre of pineapple, bamboo, hemp, jute, flax, kenaf and banana. Textile fibre based on cellulose is known as rayon, a derivate of cellulose. The aim of this research is to extract and characterize the cellulose fibre that obtained from durian rinds as the alternative of textile fibre. The characterization for the cellulose fibre including FT-IR, SEM, DSC, and XRD. The FT-IR spectra showed the heating treatment around 70-80°C can separate the lignin and hemicellulose from the durian rinds. SEM analysis showed the similar result, the heating process during the alkalization treatment able to separate lignin from the cellulose matrix, that was shown with the smoothest surface of cellulose fibre. DSC thermogram for the cellulose without heating process showed two peaks at 406 and 443°C. The lower value was obtained for the cellulose with heating process that showed at 362 and 386°C. Crystallinity degree of the obtained cellulose was 68 and 47% for without and with heating process, respectively.

1. Introduction

Cellulose is one type of biopolymer that arranged by β-D-anhidroglucopyranose through covalent bonding between C1 and C4 (β-1,4-glycosidic bond). Each functional group of β-1,4-glucopyranose bonded with 3 hydroxyl groups and formed intramolecular and intermolecular hydrogen bonding. The hydrogen bonding has a role on the properties of the characteristic of cellulose [1]. Crystallinity degree, length of polymer chain and elasticities of fibre are the factors that influenced the characteristic of cellulose fibre. The polymer structure consists of crystalline and amorph regions. Polymer with high crystallinity will form polymer that rigid and stiff.

The monomers of β-D-anhidroglucopyranose will form crystalline region and three hydroxyl group of β-D-anhidroglucopyranose has a possibility to form a crosslink that impact to the rigidness of material [2]. The length of polymer chain is depended on the degree of polymerization (DP). The polymer which has high DP will be easier to form intermolecular bonding than the low DP.
Furthermore, that is the reason why the polymer with high DP, the morphology of the fibre is more amorph [2].

Cellulose is one kind of biopolymer that abundance in nature and can be used as alternative of cotton fibre. Indonesia as an agrarian country and ranked in top five position as textile producer countries but the import value of cotton reached 99.5% [3]. The substitution of cellulose biomass as the raw material for textile is one alternative to minimalize the dependency of cotton fibre. The alternative of cellulose biomass can be obtained from non-wood and agriculture waste [1] [4]–[6].

Cellulose with some unique characteristic, such as hydrophilic, has no flavour or fragrance, not soluble in water and many of organic solvents, not only can be utilized for textile purpose but also paper, paperboard, cord stock, cellophane and rayon [6]. Lignocellulose biomass can be used for many applications depends on the chemical composition and the physic properties of lignocellulose biomass. As example, lignocellulose biomass from wheat, hemp and corn has been utilized for pulp and paper industries. Pineapple leave, banana and coconut fibre have been utilized for textile products, composites, and paper. All of those fibre has been utilized as a wood fibre substitution [7].

There is a high chance of durian rinds to be a source of cellulose fiber. Based on Indonesian Statistic Institute, in North Sumatera around 2012-2016 the production of durian almost 847.492 ton/year (“Badan Pusat Statistik,” 2017). With this number, in the next 20 years, the production of durian in North Sumatera would be 900.000 ton/year [9]. With the increase of the production of durian, the direct impact is the increase will be happened on the number of wastes of durian rinds (70-85 wt.%). Durian rinds is a bypass product after the consumption process of durian [9]–[12].

The abundance of durian rinds is a big potency for developing this fibre as the source of cellulose biomass for textile purpose. Nowadays, for the textile purpose many kinds of fibre have been utilized, such as pineapple, bamboo, hemp, jute, flax and banana. The aim of this research is to extract and analyse the morphology and crystallinity degree of cellulose from durian rinds. The analysis that has been performed such as FT-IR, SEM, DSC and XRD. The obtained data than compared to the other cellulose fibre that obtained from cotton, hemp, sisal and jute.

2. Methodology
2.1. Materials
Durian rinds was obtained from Binjai city-North Sumatera. NaOH, NaClO₄, CH₃COOH were obtained from Merck.

In this research, some equipment was used, such as glassware, analytical balance, thermometer, hot plate, oven, universal indicator, desiccator, SEM (Scanning Elektron Microscope) Quorum Model Q150R ES, FT-IR/ ATR (Fourier Transform Infrared) Bruker Opus Alpha 7.5., dan DSC (Differential Scanning Calorimetry) DSC-60.
2.2. The Extraction of Durian Fibres
Durian rinds were cleaned with water to remove any particle from its surface. Durian rinds were processed by mechanical processing until the separated fiber were obtained. The separated fiber of durian rinds were soaked in water for 1 x 24 h and washed until the surface of the separated fiber was free from gum. The obtained fiber was separated manually and dried for 3 days to remove water content (0.08%). The dried fiber was used for further analysis (Fig. 1).
2.3. Cellulose extraction

The extraction of cellulose was performed following this method [13], that has been modified. The extraction was performed through 2 steps, such as (i) the formed of holocelluloses through chlorinating or bleaching process and (ii) alkalization process.

20 g of durian rinds was added with 500 mL aquadest and 150 mL of 5% NaOCl. After 2 hours, the lignin will separate. The holocelluloses fibre were filtrated and washed with water until pH 7. The alkalization process was performed in two methods, such as with and without heating process (70-80°C). The obtained holocelluloses was soaked in 80 mL of 17.5% NaOH. Every 5 minutes into that solution 40 mL NaOH was added, this step was repeated until the total volume of NaOH reached 200 mL. After 30 minutes, 240 mL of aquadest was added into that solution and it was filtrated after 1 hour. The alkali content was neutralized with the addition of 120 mL acetic acid 10%. The cellulose fiber then filtrated, washed and rinsed until it free from acid. The cellulose fibre was dried in oven at 80°C. The yield of cellulose was calculated using the following equation:

\[
\text{Cellulose(\%)} = \frac{W_2}{W_1} \times 100\% \tag{1}
\]

Where, \(W_1\) : weight of durian rinds ; and \(W_2\) : weight of cellulose

2.4. FT-IR analysis

FT-IR analysis was performed using FT-IR spectrophotometer Bruker Opus Alpha 7.5. The analysis was performed under following condition: resolution 4 cm\(^{-1}\) and range of wavenumber 4000-600 cm\(^{-1}\). The FT-IR analysis was conducted to identify the functional group that present in durian rinds fiber.

2.5. SEM analysis

The surface morphology of durian rinds was analysed using scanning eletron microscope, Quorum Model Q150R ES. The specimen was placed in the chamber that flowed by nitrogen.

2.6. Diffrential scanning calorimetri (DSC) analysis

The stability thermal analysis of durian rinds was performed using DSC-60. The weighed sample was placed in the hermetic pans. The thermal analysis was performed in the range 30-500°C of temperature, with air flow rate 30 ml/min.

2.7. X-ray Diffraction (XRD) Analysis

The XRD analysis was performed using X-ray diffractometer (XRD-6100 Lab X-Shimadzu). The measurement condition was set at voltage 40 kV, current 30 mA and radiation of CuKα. The diffractogram of X-ray was observed in the range 2θ: 7° - 70°. The crystallinity degree of cellulose was calculated using the following equation [14]–[19].

\[
I_{cr} = \frac{I_{002}-I_{am}}{I_{002}} \tag{2}
\]

Where: \(I_{002}\) : intensity of crystallinity region; and \(I_{am}\) : intensity of amorph region
3. Results and Discussions

3.1. Extraction of durian rinds fibre

About 10 gram of durian rind was used in the extraction process. The washing process of durian rinds is conducted to remove any particle from its surface, i.e. soil or dry leave that attached on its surface. The separation process of durian rinds fibre were performed using a mechanical process. The separated fiber was soaked with water for 1x24 h, this process was performed to remove the gum and allow the biodegradation process. The fiber then dried until weight constant was obtained. The weight of the obtained fiber is 20% of weight total.

3.2. Extraction of cellulose durian rinds

Lignocellulosic biomass is a biomass that consisted by three components, such as cellulose, hemicellulose and lignin. Cellulose is surrounded by hemicellulose and lignin [20]. The extraction process of cellulose was performed to separate the lignin and hemicellulose. Cellulose durian rinds were extracted using 2 steps (Figure xx), such as delignification using NaClO2 and alkalization process using NaOH with and without heating process. The cellulose that obtained without heating process has yield of 47.95% (Cell I) and 42.7% that obtained with heating process (Cell II). There is a difference about 5.25% on the yield of both cellulose, this indicated the heating process has an important role in the extraction process to remove the hemicellulose and lignin. The obtained yield showed a similar value with the cellulose that obtained from cotton (58%) and sorghum (41.5%) [21]

3.3. FT-IR analysis

FT-IR analysis of durian rinds (Fig 3) was conducted to determine the band of cellulose, hemicellulose and lignin. The obtained band was compared to cellulose that isolated from other fibre (Table 1).

| Vibration          | Cell I (cm\(^{-1}\)) | Cell II (cm\(^{-1}\)) | Hemp\(^{\#}\) (cm\(^{-1}\)) | Sisal\(^{\#}\) (cm\(^{-1}\)) | Jute\(^{\#}\) (cm\(^{-1}\)) | Kapok\(^{\#}\) (cm\(^{-1}\)) |
|--------------------|----------------------|------------------------|-------------------------------|--------------------------|------------------------|---------------------------|
| stretching         | 3318.41              | 3323.03                | 3447-3449                     | 3447-3448                | 3448-3474              | 3407-3421                 |
| C=O vibra          | 2875.91              | 2912.27                | 2893-2901                     | 2930                     | 2915-2998              | 2916-2918                 |
| C=C stretching     | 1629.68              | -                      | 1638-1654                     | 1636                     | 1636                   | -                         |
| C-H bending        | 1313.81              | 1336.68                | 1382-1384                     | 1384                     | 1384                   | 1383-1381                 |
| C-H stretching     | -                    | -                      | 1248-1250                     | -                       | -                      | -                         |
| C-C stretching     | 1023.43              | 1028.94                | 1000-1162                     | 1000-1162                | 1000-1162              | 1000-1162                 |
| -OH                | 523.59               | 509.07                 | 667-670                       | -                       | 668                    | 609-668                   |

\(^{\#}\)FT-IR analysis [23]

The FT-IR analysis of Cell I and Cell II showed specific bands for O-H and C-H stretching around 3300 and 2870-2910 cm\(^{-1}\). The significance result was shown in Sel I spectra at 1630 cm\(^{-1}\) that indicated the presence of C=C stretching from benzene structure of lignin. The other work showed the presence of lignin was indicated by the presence of several band at 1830 and 1730 cm\(^{-1}\) that referred to methoxy (OCH\(_3\)), C-O-C and C=C aromatic. The presence of signal at 1313 and 1336 in the Cell I and Cell II indicated the presence of hemicelluloses [14] [22]. The other signal at 1023 -1028 indicated the presence of CH, OH or CH\(_2\) stretching.

3.4. SEM analysis

The morphology of Cell I and Cell II was observed using Scanning electron microscopy (SEM) with the magnification of 50, 100 and 200x. The Fig. 3 and 4 showed the microphotograph of cellulose fibre Cell I (without heating treatment) and Cell II (with heating treatment), respectively. Fig. 4 showed the obtained cellulose has smoother surface than cellulose in Fig 3. This indicated that lignin was successfully separated in the cellulose with heating process than without heating process. The
presence of lignin is showed as a bundle of fibre that not well separated. The fibre width of Cell I is 15,446 µm and the Sel II is 14,384 µm, this different value is caused by the reduction of lignin content. This reduction in the number of width will improve the L/D ratio [13].

Figure 2. Scanning elektron micrograph of cellulose without heating process (Cell I) with magnification; (a) 50 x, (b) 100 x, dan (c) 200x
3.5. DSC analysis

Thermal analysis, differential scanning calorimetry (DSC), of Cell I and Cell II was performed to measure the stability thermal of cellulose from durian rinds. Thermal degradation has a big influence to the supramolecular structure of cellulose [23]. Thermal degradation can be observed based on the endotherm and exotherm reaction of cellulose. Table 2 showed the endotherm and exotherm also the heat process of Cell I and Cell II.

| Sample   | Exotherm (°C) | Endotherm I (°C) | Endotherm II (°C) |
|----------|---------------|-----------------|------------------|
|          | Peak          | ΔH (J/g)        | Peaks            | ΔH (J/g) | Peak          | ΔH (J/g) |
| Cell I   | 80.66         | -234.17         | 406.79           | +19.83   | 443.63        | +29.88   |
| Cell II  | 85.73         | -150.92         | 362.55           | +14.96   | 386.54        | +3.53    |

The alkalization process has a role to remove the lignin and hemicellulose content in durian rinds fibre. The separated of lignin and hemicellulose reduce the number of amorph region in cellulose and increase the number of crystalline region [24]. The increase in crystalline region has an influence on the thermal degradation process, especially increase the degradation temperature. DSC thermogram of Cell I and Cell II showed the presence of exotherm and endotherm peak. Endotherm peak indicated the degradation of cellulose molecule. In the Cell I, the endotherm peak was found at 406 and 443°C but in Cell II, it was found at 362 and 386°C. The different of endotherm peak value indicated the successfully of lignin and hemicellulose separation for Cell II than Cell I.
3.6. XRD (X-ray diffraction) analysis

XRD analysis was performed to determine the crystallinity degree of obtained cellulose, the diffractogram was shown in Fig 6. XRD diffractogram showed the obtained cellulose has crystalline and amorph region. The crystallinity of each fibre was shown in Table 2. The different of that value was influence by the different on the alkalinization process.

This result indicated the extraction of cellulose during the alkalinization process with the heating process is more effective to separate lignin and hemicellulose matrix than without heating process. Lignin and hemicellulose are polymer with amorph phase. The removal of those components from the cellulose fibre led to the increase of crystallinity degree. In this work, the crystallinity of the Cell I is higher than Cell II, it can be caused by the influence of heating process that led to the depolymerization of cellulose. This depolymerization structure of cellulose influences the crystallite size [24]. The obtained cellulose has similar properties with the cellulose that obtained from any kind of sources, such as hemp, sisal, cotton, banana, etc.

| Sample   | (2θ) (Degree) | FWHM (Degree) | Intensity (Count) | Index crystallinity (Ic) /% |
|----------|---------------|---------------|-------------------|-----------------------------|
| Cell I   | 22,3416 | 1,73670 | 9027             | 68,29682                   |
|          | 64,6000 | 0,56800 | 1860             |                            |
|          | 44,2613 | 0,57070 | 1486             |                            |
| Cell II  | 44,6234 | 0,19010 | 1728             | 47,07213                   |
|          | 64,9285 | 0,18470 | 1719             |                            |
|          | 9,4850  | 0,24340 | 408              |                            |
4. Conclusion

The alkalization process on plant fibers can change the topography of the fibre and the crystallography of fibre. The temperature of alkalization process has a big influence on the rate of alkalization. The obtained result showed that the obtained cellulose from two types alkalization process has different properties (FT-IR, SEM, DSC and XRD). The FT-IR spectra of Cell II showed that the alkalization with heating process was success to remove lignin and hemicellulose from the cellulose matrix. SEM microphotograph showed the Cell II has a smoother surface than Cell I, indicated the lignin was removed from the matrix. The DSC thermogram of Cell I was 406 °C and 443°C, Cell II was 362 °C and 386°C. The crystallinity degree of Cell I and II was 68% and 47%. The obtained cellulose has similar properties with the cellulose that obtained from any kind of sources, such as hemp, sisal, cotton, banana, etc.

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