Modification of Pulp Cellulose of Belangke Bamboo (*Gigantochloa pruriens*) using [2-(Acryloyloxy)Ethyl] Trimethyl Ammonium Chloride and Maleic Anhydride

Rina Ridara[1], Diana Adnanda Nasution[2] and Basuki Wirjosentono[2*]

[1]*Postgraduate Chemistry Study Program, Faculty of Mathematics and Natural Sciences, Universitas Sumatera Utara, Jl. Bioteknologi No. 1 Kampus USU, Medan, Indonesia*

[2]*Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Sumatera Utara, Jl. Bioteknologi No. 1, Medan 20155, Indonesia*

Keywords: Cellulose, Belangke Bamboo, Modification, Antimicrobial Compound.

Abstract: In this work, pulp cellulose (Cell) was prepared from Belangke bamboo (*gigantochloa pruriens*) by Craft delignification process. The AETAC/MA-modified Cellulose (AETAC/MA-g-Cell) was characterised using infrared spectroscopy (FTIR) for chemical structure, differential scanning calorimetry (DSC) for thermal properties and scanning electron microscopy (SEM) for morphological images. Results of FTIR spectra of the AETAC/MA-g-Cell after exhaustive Sokhlet extraction in n-hexane still showed stable absorption peak of AETAC/MA carbonyl group (>C=O) at 1705 cm^{-1} and disappearance of double bond absorption peak af acryloyl group (>C=C<) at 1630 cm^{-1}. These evidences indicated that the AETAC/MA modifiers have successfully bound into the cellulose, in which hydroxyl groups of the cellulose have esterified with maleic anhydride and bound with acryloyl groups of AETAC. Further data of DSC analysis of the modified cellulose showed slightly lower decomposition temperature of 300ºC when compared to that of fresh cellulose of 270-400ºC. Whereas SEM images of the modified cellulose also indicated rougher surface when compared to that of fresh cellulose fibres. The AETAC/MA-modified cellulose then may be utilised as antimicrobial materials for various cellulose products.

1 INTRODUCTION

Indonesia is a tropical country rich in non-timber crops that can be used as an alternative raw material for the pulp and paper industry. One type of non-timber plant is bamboo. Bamboo is a general term for members of the wooden grass, the Bambusoideae subfamily and the Andropogoneae / Poacea family. Bamboo has several advantages compared to woody plants that grow fast and can be harvested after 3-5 years of planting, much shorter than needle wood which takes 10-20 years. In addition, bamboo has high productivity and can grow in arid soils (My & Le, 2015). As a non woody plant, bamboo is known for its long fiber with an average fiber length of 1.90-3.24 (Tian, 2013).

Bamboo is grass, cylindrical in shape which is mostly hollow (though some species are solid cylindrical). Bamboo usually has a height of 20-25 meters. Biomass production in the planting season is around 3-5 months. Bamboo consists of 26-43% cellulose, 21-31% lignin, and 15-26% hemicellulose. In theory, the mechanical properties of bamboo mainly depend on (1) species, (2) age, (3) moisture content, (4) position along the stem (top or bottom), and (5) node and segment position. Belangke bamboo (*Gigantochloa pruriens*) which is 125 species of bamboo in Indonesia can grow to 10 meters in length with a diameter of 5 cm and a length of 35 cm. This type of bamboo has been used by the community for various household, equipment, construction and handicraft industries. Textile fibers made from bamboo are still not popular, and even more than 1500 species of bamboo in the world, only a few types are processed into textile materials (Waite, 2009).

However, given its availability, especially in Indonesia which is abundant, the prospect of bamboo fiber as a textile material for clothing is quite promising compared to other natural fibers. Nowadays, the use of antimicrobial textile materials has been growing, due to the people's perception of

Ridara, R., Adnanda Nasution, D. and Wirjosentono, B.
Modification of Pulp Cellulose of Belangke Bamboo (Gigantochloa pruriens) using [2-(Acryloyloxy)Ethyl] Trimethyl Ammonium Chloride and Maleic Anhydride.
DOI: 10.5220/0008932303050311
In *Proceedings of the 1st International Conference on Chemical Science and Technology Innovation (ICOCSTI 2019)*, pages 305-311
ISBN: 978-989-758-415-2

using hygienic and clean textile materials which is increasing. Textile materials, especially for underwear, are indeed susceptible to exposure, and can even be a living medium for microbes, which cause these textile materials: easy to smell, have spots, and damage (Kumar, 2011).

Cellulose is one of the most widely dispersed, renewable, and biodegradable polymers. Cellulose is a natural polymer that does not dissolve in water due to long chains and high molecular weight (more than 500,000 Da) (Fathanah, Lubis, Othman, Handayani, & Karlina, 2017).

Cellulose is the main element of all plant material, forming about half to one third of all plant tissue and is constantly formed from photosynthesis (Sun, Sun, Zhao, & Sun, 2004). This is the main structural component that provides strength and stability to plant cell walls which are arranged in microfibrils in cell walls, interrupted by hemicellulose and surrounded by a lignin matrix. Depending on the type of plant, most plant material consists of about 40 - 55% cellulose, 15 - 35% lignin and 25 - 40% hemicellulose. On the cell wall of natural plants, cellulose crystals are covered with these substances which makes it difficult to get pure cellulose. Chemically, cellulose is a naturally occurring linear polymer of anhydroglucose unit connected to one and four carbon atoms by β-glycosidic bonds. It is proven by the presence of three hydroxyl (OH) groups with different acidity / reactivity, where secondary OH is located in the C-2, and C-3 positions, and the primary OH is located in the C-6 position. This is also verified by the formation of various strong hydrogen bonds between molecules and intramolecules (Penjumras, Abdul, Talib, & Abdan, 2014). In recent years, interest in cellulose-based materials has increased due to the demand for renewable resources (Mohanty et al., 2005).

MA grafting into various polymers has been popular for the past 20 years. Grafted copolymers can be used as the main component. Various polymers have been used as backbones for grafting maleic anhydride. Other types of thermoplastics (PS, EVA, PES), as well as elastomers (EPDM, EPR, NR), can also be used as polymers for MA grafting (Krump, Alexy, & Luyt, 2005).

As is known, 2-acryloyloxyethyl trimethyl ammonium chloride (AETAC) consists of quaternary ammonium salt groups and unsaturated vinyl groups. Vinyl groups can be polymerized and can react with a variety of vinyl monomers, which in 2016 Shen et al conducted research on poly [(2-acryloyloxyethyl trimethyl ammonium chloride) -co-(acrylic acid)] branches onto starch for cotton warp sizing (Shen, Zhu, & Liu, 2016).

Wool fiber antimicrobial textile material has been developed using a coating technique with a bioactive polymer material, [2- (acryloiloxy) ethyl] trimethylammonium chloride (AETAC). Antimicrobial properties of wool fiber coated with bioactive polymers were tested against Gram-positive and Gram-negative bacteria, Staphylococcus aureus and Klebsiella pneumoniae. Furthermore, the surface morphology characteristics of the fibers were tested using reflected infrared spectroscopy (ATR-FTIR), electron microscopy (SEM), tensile strength and contact angle to water drops. the result is that Q-chitosan-based antibacterial properties against wool can be improved by grafting wool fabric with polystyrene sulphonate (pSS), which shows very good antibacterial activity against Staphylococcus aureus and Klebsiella but less good against the fungus Aspergillus fumigatus. Transplanting a wool fabric with pSS not only increases the tensile strength of the fabric but also increases the durability of the treatment of several washings. pSS-g-wool, Q-chitosan evenly covers the surface of the treated fiber and after 5x the washing is still intact. Therefore this grafting process is commercially viable for wool fabrics (Hassan, 2015).

The two most common methods used to analyze thermal properties are thermogravimetric analysis (TGA) and (DSC). The TGA technique measures the weight loss and mass change of a substance as a function of temperature. However, there are several reactions that can occur without mass loss. In this case, DSC is able to detect these reactions (Zakikhani, 2016).

In this research, the surface modification of cellulose fiber from Belangke bamboo will be modified with antimicrobial compound (AETAC), with the help of maleic anhydride (AM) and ammonium persulfate as comonomer and initiator. Furthermore, the surface morphology characteristics of the fibers were tested using reflected infrared spectroscopy (ATR-FTIR), electron microscopy (SEM), Thermal Analysis Differential Scanning Calorimetry (DSC).

2 MATERIALS AND METHODS

2.1 Materials

The material used in this study is 80% solution of 2-(acryloyloxy)-ethyltrimethylammonium chloride were purchased from Sigma-Aldrich Chemicals (USA) and used without any purification, ammonium persulfate

$(NH_4)_2SO_4$ ≥90% from China, maleic anhydride with weight molecul 98.06 g/mol, acetone and toluene from Mallinckrodt Chemicals (USA). Belangke bamboo that is used comes from Pangkalan Brandan, Sei Lepan Subdistrict, Langkat Regency, North Sumatra, located on the east coast of the island of Sumatra, about 60 km north of Binjai City.

2.2 Methods

2.2.1 Preparation of Belangke Bamboo

The bamboo Belangke obtained is washed with water until clean then dried in the sun to dry then cut with a grinding cutter until it becomes powder.

2.2.2 Isolation of α-cellulose from Belangke Bamboo

As much as 75 grams of Belangke Bamboo Powder then put into a glass beaker and added 1 L mixture of 3.5% HNO_3 and 10 mg $NaNO_2$ heated on a hot plate at 90ºC for 2 hours. After that filtered and washed pulp until neutral filtrate. Then added with 750 ml of solution containing 2% of NaOH and 2% of Na_2SO_3 at 50ºC for 1 h then filtered and washed pulp until neutral filtrate. Then bleaching with 500 ml of 1.75% of NaOCl solution at boiling temperature for 30 minutes. The pulp is filtered and washed until neutral filtrate. After that, α-cellulose was purified from a sample of 500 ml of 17.5% NaOH solution at 80ºC for 0.5 hours then filtered, washed until neutral filtrate. Continuing bleaching with 10% H_2O_2 at 60ºC for 15 minutes. Washed and filtered cellulose to neutral. Oven drying was carried out for 3 hours at 60ºC and stored in a desiccator (Ohwoavworhua, 2005). Characterization of α-cellulose produced includes: % yield, chemical-physical properties analysis, functional groups (FTIR), morphology (SEM), thermal analysis (DSC).

2.2.3 Modification of α-cellulose with Maleic Anhydride

Modification of α-cellulose bamboo belangke with maleic anhydride was done by reflux for 2 hours using toluene as a medium. Reaction optimization was carried out with fixed cellulose levels (100 phr) with maleic anhydride variations (5, 10, 15, 20 phr).

The toluene solvent was evaporated at 110ºC, then washed with acetone to remove free maleate. The result of cellulose / AM is dried in an oven at 70ºC until the weight remains, then characterized by functional group analysis (FTIR).

2.2.4 Modification of Cellulose Fibers with [2-(Acryloiloxy) Ethyl] Trimethyl Ammonium Chloride (AETAC)

Surface modification of Belangke bamboo cellulose fibers with [2- (acryloyloxy) ethyl] trimethylammonium chloride (AETAC) 80% was carried out in the reflux phase modification reactor and stirring with toluene solvent and the addition of maleic anhydride (AM) and ammonium persulfate as comonomers and initiators. Reaction optimization was carried out by varying the levels of maleic anhydride and AETAC reagent levels by adding 10% ammonium persulfate from the optimum level of maleic anhydride. The toluene solvent was taken back by a vacuum evaporator and the AM-AETAC-modified cellulose was dried in a 70ºC vacuum oven to a fixed weight. Characterization of α-cellulose modified with [2- (acryloyloxy) ethyl] trimethylammonium chloride (AETAC) produced included: functional groups (FTIR), morphology (SEM), thermal analysis (DSC).

3 RESULTS AND DISCUSSION

3.1 Isolation of α-cellulose from Belangke Bamboo

Based on a series of delignification, swelling and whitening processes that have been carried out in this study in order to obtain white α-cellulose. At the isolation stage, α-cellulose is used 75 grams of belangke bamboo powder and at the end of the process produces pure α-cellulose of 10.95 grams (as much as 14.6% of the initial weight of belangke bamboo used). Figure 1: shows the α-cellulose results obtained from this study.

Figure 1: α-cellulose powder isolated from bamboo belangke.

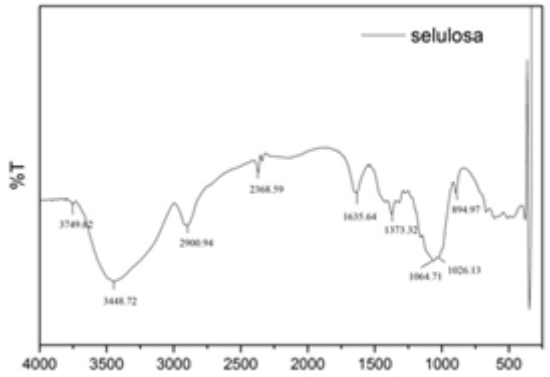

Figure 2: FTIR spectrum of cellulose.

Functional group analysis with FT-IR has been carried out, for the cellulose spectrum shown from FT-IR data to provide cellulose support that has an -OH group with the emergence of vibration peaks at wave number 3448.72 cm^{-1} and supported by peak absorption at wave numbers 1026.13 cm^{-1} which shows the vibration of the symmetric CO group and the absorption peak at wave number 1373.32 cm^{-1} shows the anti-symmetric CO vibrations. The peak vibrations at wave number 2900.94 cm^{-1} are stretching C-H vibrations supported by bending C-H vibrations at wave number 671.23 cm^{-1}. The emergence of the vibration peak at wave number 2368.59 cm^{-1} shows the C-C stretching vibration and is supported by the wave number 894.97 cm^{-1} which shows the C-C bending (Penjumras et al., 2014).

3.2 Modification of Belangke Bamboo Cellulose α-Maleic Anhydride

In order to optimize the conditions for grafting of maleic anhydride onto cellulose, we did this by varying the concentration of monomers. The grafting mechanism of anhydride groups onto cellulose in the melt, it has been shown that the grafted polymer generally contains residual amounts of free (ungrafted) maleic anhydride as well as free ungrafted polymaleic anhydride sequences. It has been shown that the free maleic anhydride can be removed by vacuum-drying while the free polymaleic anhydride is removed by washing. Cellulose grafting with maleic anhydride can be calculated from the peak FTIR characterization. Because the absorption coefficient was calculated, the content of the grafted maleic anhydride onto the cellulose form can simply be determined by measuring the FTIR spectra (Krump et al., 2005).

Table 1: Cellulose grafting results with variations in the concentration of maleic anhydride.

Cellulose (php)	Maleic anhydride (php)			
100	5	10	15	20
13.6544	0.0269	0.0775	0.1612	0.1131

From the data in Table 1 it appears that the optimum conditions for the addition of maleic anhydride at 15 phr. This shows that the increase in the degree of grafting caused by the cross-ring formation of polymers and poly (maleic anhydride) increases. the degree of grafting begins to decrease when the concentration of maleic anhydride is more than 15 phr, this is due to the homopolymerization that causes maleic anhydride monomers tend to form a polymer themselves compared to sticking to cellulose.

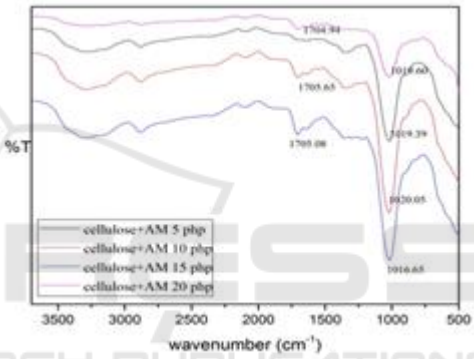

Figure 3: FTIR spectrum of α-cellulose with various AM levels.

From the data in Table 2: it can be seen that the optimum conditions of adding AETAC to 20 phr are 0.6393, when the addition of AETAC 30 phr to the condition of grafting decreases. This is because the number of AETAC additions causes the reaction between maleic anhydride and cellulose not to the maximum possibility of maleic anhydride monomers with less colliding cellulose. Grafting is increased if maleic anhydride monomers with cellulose and AETAC collide with each other.

Figure 4 shows the results of grafting between the optimum conditions of AM-cellulose produced previously with variations in AETAC levels. Of the three FTIR results obtained, all three AM-cellulose have been successfully grafted with AETAC. This can be seen with the emergence of new peaks at wavelengths of 1463, 1465 and 1467 cm^{-1} which are the tops of the methyl groups of antimicrobial compounds (AETAC). But after calculating the surface area by using the previous formula which

compares the peak of maleic anhydride with one of the cellulose peaks, it can be produced that the optimum condition of cellulose-AM-AETAC modification is on the addition of 20 php AETAC.

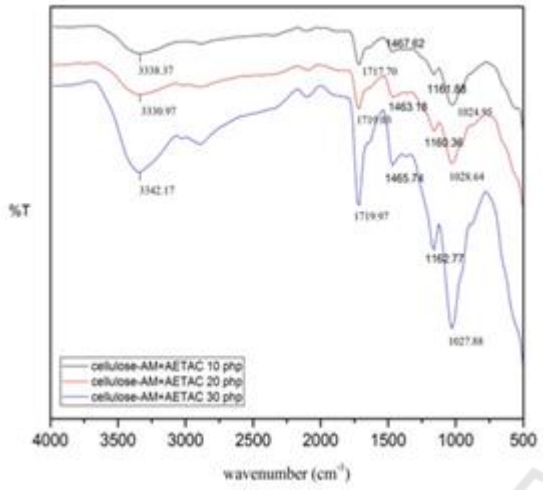

Figure 4: FTIR spectrum of α-cellulose-AM with various AETAC levels.

3.3 Analysis Results Scanning Electron Microscope (SEM)

The results of the SEM analysis can provide information about the shape and change of the material being tested. In principle, if there is a change in a material such as fractures, indentations, and structural changes, the material tends to experience energy changes. The changed energy can be emitted, reflected, and absorbed and converted into electron waves that can be captured and read the results on SEM photographs.

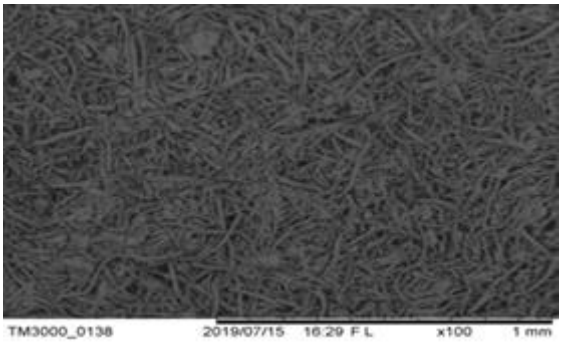

Figure 5: SEM test results of bamboo cellulose surface with 100x magnification.

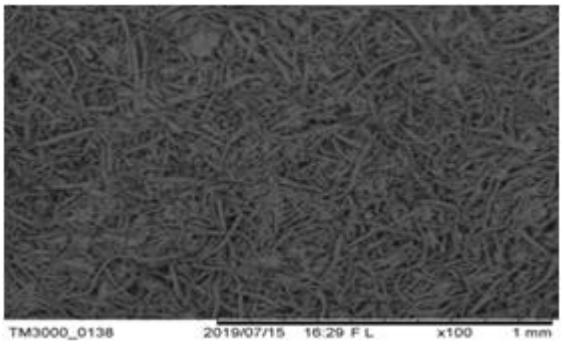

Figure 6: SEM test results of bamboo cellulose surface with 500x magnification.

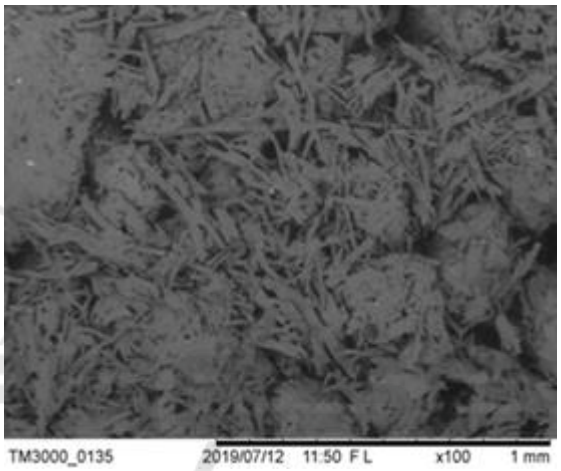

Figure 7: SEM test results for MA-AETAC cellulose grafting with 100x magnification.

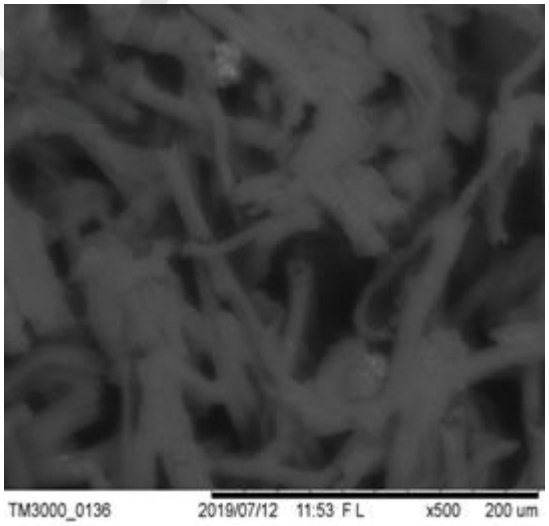

Figure 8: SEM test results for MA-AETAC cellulose grafting with 500x magnification.

The SEM results shown Figure 7: shows that the structure is uniform, homogeneous and has small pores which are cellulose structures from bamboo belangke. Cellulose has an ion -OH bond that can cause the adsorption process.

Figure 8: shows that the structure of cellulose has changed due to the addition of maleic anhydride and aetac. These changes state that the surface of cellulose has been grafting maleic anhydride and aetac, there are some areas where clots occur and enlarged pores.

3.4 Differential Scanning Calorimetry (DSC) Analysis

DSC analysis is used to study phase transitions, such as melting, glass transition temperature (Tg) or exothermic decomposition and to analyze the stability of oxidation and heat capacity of a material. A technique used to determine the temperature of a material transformation by quantifying its heat. The data generated in the form of a heat flow curve to the sample minus the heat flow to the reference to time or temperature.

In thermal analysis, cellulose decomposes at temperatures between 270oC to 400oC. In this area, cellulose decomposes into D-glucopyranose monomers (Yang, 2008). This can also be seen in Figure 5: which shows that cellulose is degraded at 400oC and also on the DSC results of cellulose modification with AM-AETAC degradation at 300oC.

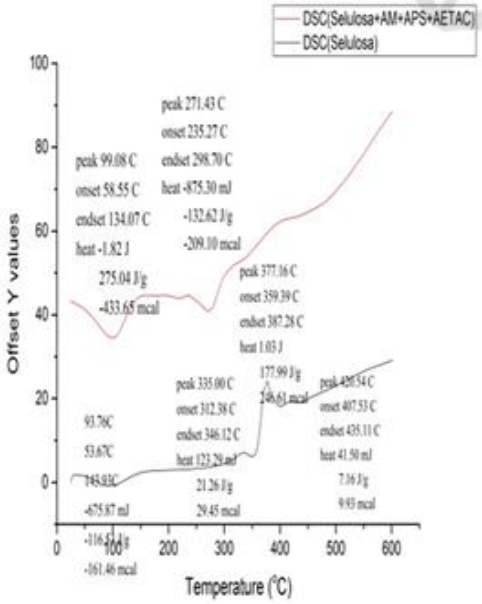

Figure 9: DSC analysis of cellulose and cellulose / AM-AETAC.

4 CONCLUSIONS

Optimization and reaction mechanism of the modification process and surface characteristics of cellulose pulp from Belangke bamboo with the help of maleic anhydride through FTIR test that is found in the addition of 15 phr maleic anhydride by calculating the surface area of FTIR which compares the peak of maleic anhydride with one of the peaks of cellulose.

Characterization of functional groups (FTIR), morphology (SEM) and thermal strength (DSC) of cellulose, cellulose / AM and AM-AETAC cellulose grafting namely the emergence of new and characteristic peaks from cellulose and from maleic anhydride. The change in cellulose morphology to cellulose grafting AM-AETAC is marked by a change in the surface structure in the form of pores, indentations and faults. In thermal analysis, cellulose decomposes at temperatures between 270^{o}C to 400^{o}C. In this area, cellulose decomposes into D-glucopyranose monomers. This can be seen from the endothermic and exothermic reactions that occur. The FTIR results can be calculated the optimum conditions from the addition of AETAC, namely by calculating the surface area of the peak maleic anhydride with one of the cellulose peaks obtained the optimum conditions for the addition of AETAC of 20 phr.

ACKNOWLEDGEMENTS

Authors would like to thank to Ministry of RISTEK-DIKTI, the Republic of Indonesia for financial support through DRPM program 2018. Furthermore, additional support from all those who helped the completion of this research are gratefully acknowledged.

REFERENCES

Fathanah, U., Lubis, M. R., Othman, N., Handayani, M. N., & Karlina, S., 2017. Preparation and Characterization of Cellulose and Nanocellulose from Agro-industrial Waste - Cassava Peel Preparation and Characterization of Cellulose and Nanocellulose from Agro-industrial Waste - Cassava Peel. https://doi.org/10.1088/1742-6596/755/1/011001

Hassan, M. M., 2015. Binding of a quaternary ammonium polymer-grafted-chitosan onto a chemically modified wool fabric surface: Assessment of mechanical, antibacterial and antifungal properties. RSC Advances,

5(45), 35497–35505. https://doi.org/10.1039/c5ra03073k

Krump, H., Alexy, P., & Luyt, A. S., 2005. Preparation of a maleated Fischer – Tropsch paraffin wax and FTIR analysis of grafted maleic anhydride, 24, 129–135. https://doi.org/10.1016/j.polymertesting.2004.09.011

Kumar, G. V., 2011. Studies on Antimicrobial Textile Finish Using Certain Plant Natural Products, 560059(9980819835).

Mohanty, A., Misra, M., Drzal, L., Selke, S., Harte, B. R., & Hinrichsen, G., 2005. Natural fibers, biopolymers, and biocomposites: An introduction. In Natural Fibers, Biopolymers, and Biocomposites (pp. 1–36).

My, T., & Le, A., 2015. Overview of bamboo biomass for energy production to cite this version: 0–24.

Ohwoavworhua, F. O., & Adelakun, T. A., 2005. Phosphoric Acid-Mediated Depolymerization and Decrystallization of α - Cellulose Obtained from Corn Cob: Preparation of Low Crystallinity Cellulose and Some Physicochemical Properties, 4(December), 509–516.

Penjumras, P., Abdul, R. B., Talib, R. A., & Abdan, K., 2014. Extraction and Characterization of Cellulose from Durian Rind. Italian Oral Surgery, 2, 237–243. https://doi.org/10.1016/j.aaspro.2014.11.034

Shen, S., Zhu, Z., & Liu, F., 2016. Introduction of poly [(2-acryloyloxyethyl trimethyl ammonium chloride) - co - (acrylic acid)] branches onto starch for cotton warp sizing. Carbohydrate Polymers, 138, 280–289. https://doi.org/10.1016/j.carbpol.2015.11.058

Sun, J. X., Sun, X. F., Zhao, H., & Sun, R. C.,2004. Isolation and characterization of cellulose from sugarcane bagasse. Polymer Degradation and Stability, 84, 331–339. https://doi.org/10.1016/j.polymdegradstab.2004.02.008

Tian, C., 2013. Improvement in the Fock test for determining the reactivity of dissolving pulp. Tappi Journal (Vol. 12).

Waite, M., 2009. Sustainable Textiles: The Role of Bamboo and a Comparison of Bamboo Textile Properties, 6(2), 1–21.

Yang, Z., Xu, S., Ma, X., & Wang, S., 2008. Characterization and acetylation behavior of bamboo pulp. Wood Science and Technology (Vol. 42). https://doi.org/10.1007/s00226-008-0194-5

Zakikhani, P., Zahari, R., Sultan, M. T. H., & Majid, D. L., 2016. com Thermal Degradation of Four Bamboo Species, 11(Yu 2007), 414–425.