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MANUFACTURING AND CHARACTERIZATION OF PHYSICAL PROPERTIES AND BIODEGRADABLE OF CELLULOSE NANOFIBER COMPOSITES WITH POLYMER MATRIX

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ABSTRACT

Research has been carried out on the characterization of the physical and biodegradable properties of areca nut nanofiber composites with a polymer matrix with the aim of understanding the physical factors that affect the mechanical strength and biodegradability of the composite material. The method of making nanocellulose from betel nut is fiber refining, bleaching, and delignification which are then homogenized. The composite was made by dry mixing method between nanocellulose and polymer. The tests carried out are in the form of physical properties tests (tensile strength, strain, modulus of elasticity, and biodegradation tests) and tests of electrical properties (conductivity). The characterizations used are PSA (Particle Size Analyzer), FTIR (Fourier Transform Infrared), and transparency test. The results obtained in the form of the highest tensile strength, strain, and modulus of elasticity were 11.23 MPa, 52.17%, and 21.252 MPa. The average value of biodegradation is 4.0008033%/day. The highest conductivity value is 3.2 x 10-4 S/cm. The results of PSA characterization showed that the nanofibers had a particle diameter of 79-187 nm. FTIR characterization shows that there are C=O functional groups and C-O on the plastic film is a hydrophilic group which indicates that the plastic film can be degraded.

Keywords: Cellulose nanofibers; areca nut shell; conductivity; film composites.

INTRODUCTION

Natural fibers can be classified based on their source, namely natural fibers derived from animals and plants. Indonesia has areas with suitable climatic conditions for the development of natural fibers, such as Sulawesi, Kalimantan and Sumatra. Natural fiber is a renewable material so that agribusiness from natural fiber is a sustainable and environmentally friendly business (Aryal et al., 2019; Binoj et al., 2016). Natural fibers have expanded their use in various sectors such as the textile industry, electronics, and the automotive sector.

One of the natural fibers that have the potential to be developed in tropical countries such as Indonesia is areca nut. Areca nut is very easy to cultivate with a

harvest season once every six months. In order to be a good filler in composites, areca fiber certainly needs to be reduced in size to micro and even nanoscale through chemical, mechanical, or a combination of both processes (Battistelli et al., 2020; Hosseini, 2017). This process serves to remove the hemicellulose and lignin content contained in the cellulose fiber walls, as well as to decompose the fibers into smaller sizes. Smaller fiber size can increase the surface area or contact area of the composite matrix material which affects the mechanical properties of the composite (Shanmugasundaram et al., 2018; Yusriah et al., 2014). In addition to the size of the fiber diameter, the high cellulose content in betel nut is also believed to be one of the reasons it has high mechanical properties.

In addition to the research above, several other studies on the use of betel nut as a filler in epoxy matrix composite materials have been carried out (Banagar et al., 2018; Dynanty & Mahyudin, 2018). However, there has been no research on cellulose from betel nut as a filler in epoxy matrix composite materials, especially areca nut fibers obtained from West Sumatra. The studies mentioned above examined the effect of the percentage of areca fiber on the mechanical strength of composite materials.

In this work, cellulose from betel nut fiber will be developed as a filler in an epoxy matrix composite material, so as to increase the mechanical strength and biodegradability of the composite material. For the initial stage of this proposal will be extracted cellulose from betel nut using the method of Abe (Abe et al., 2007). In the second stage, this study applied cellulose as a filler in composite materials using the hand lay up method and polymer blend with volume fraction variations of 5%, 10%, 15%, 20%, and 25%. The tests carried out include the tensile strength test, and the biodegradation of the composite material. Physical properties that affect the strength of composite materials will be investigated by characterizing FTIR (Fourier Transform Infrared) and PSA (Particle Size Analyzer).

METHODOLOGY

1. Experiments

a. Material and Method

Dried areca nut skins were collected from Pariaman, Payakumbuh, and Sijunjung Regencies in West Sumatera. The fibers were separated from the skin manually for extraction to obtain cellulose nanofiber. Materials used in the extraction process are: (1) N-hexane and ethanol for the dewaxing stage, (2) $NaClO_2$ and CH_3COOH for the bleaching stage, (3) H_2SO_4 for the acid hydrolysis stage.

b. Isolation of Cellulose Nanofiber

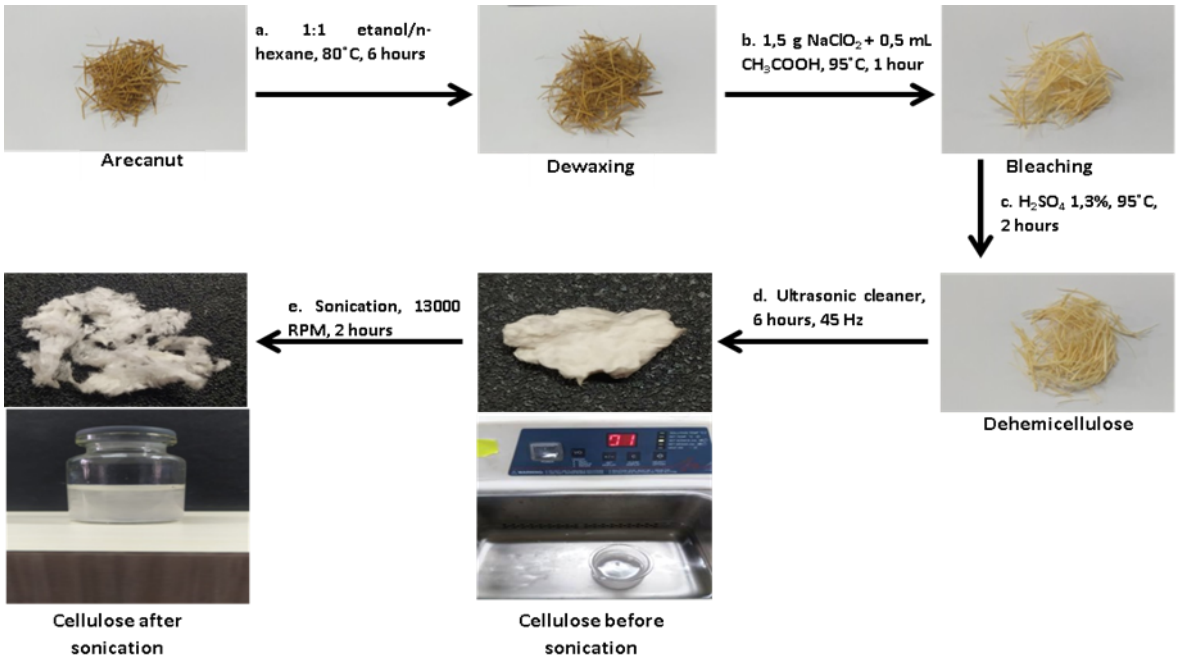

Figure 1. Procedure for preparing cellulose nanofibers from areca nut skin.

The flow chart of the overall cellulose nanofiber isolation processes is shown in Figure 1. The dried fibers were cutinto short fibers with a length of 1 cm. Areca fibers were dried and dewaxed in a mixture of (1:1, v/v) ethanol and nhexane for 6 hours at 80 °C followed by neutralization with distilled water and dried in an oven at 105 °C for 3 h. The extracted areca nut fibers were then blended as much as 2 g, put in a 500 mL Erlenmeyer flask, 1.5 g of $NaClO_2$ and 0.5 mL of CH_3COOH were added and heated at 950 °C for 1 h to remove the lignin layer (Kalia et al., 2011). After 1 h, 1.5 g of $NaClO_2$ and 0.5 mL of CH_3COOH were added again with repeated additions carried out for a total time of 4 h. The bleached areca nut fibers were neutralized using distilled water at 40 °C and dried in an oven at 1050 °C for 3 h. The bleached fiber was then put into a 500 mL Erlenmeyer flask, added 200 ml H_2SO_4 1.3% heated at a temperature of 950 °C for 2 h to remove the hemicellulose content (Akinjokun et al., 2021; Chakravarthy et al., 2020). After the addition of H_2SO_4, cellulose was produced. The obtained cellulose was then purified with distilled water. The obtained cellulose fibers were mechanically processed using ultrasonication method (ultrasonic cleaner Bransonic 3510E-DTH, frequency 42 kHz, power output 100 W) for 6 h at a temperature of 70 °C. Cellulose fiber 2% (w/v) from 50 mL of distilled water was put in a glass beaker then ultrasonicated at 18000 RPM for 2 h using a mini homogenizer (MIULAB MT-13K0L output voltage 3 V, power 0.9 W).

c. Nanocellulose Composite Film Manufacturing

Thin film composites have been formed using nanocellulose and polyvinyl alcohol (PVA). The nanocellulose used is nanocellulose which has been homogenized and filtered using filter paper. PVA crystals (1.5 g) were dissolved in 15 ml of distilled water and the mixture was heated at 80 °C for 2 hours and cooled. Nanocellulose was added to it with variance proportions of 10%, 20%, 30%, 40%, and 50% by weight (w/w) PVA. Mixing was carried out using a stirrer for 2 hours. The material is printed on glass which is placed in an aluminum plate with a size of 7.5 cm x 2.5 cm x 0.5 cm. The composite film was dried in an oven for 5 hours at a temperature of 65 °C. The dried composite films were left for 28 days.

d. Conductivity Test Sample Composite Manufacturing

The conductivity test sample composites were formed with areca nut, polyaniline (PANi), and titanium dioxide nanofiber by dry mixing method. The areca nut nanofiber variations were 3%, 5%, and 7% of the mold volume, respectively. The PANi used in each sample is 70% of the mold volume and the rest is titanium dioxide. After mixing, the test sample composites were molded into tablets with a diameter of 0.5 cm, a thickness of 1 cm and the composite was ready to be used for testing electrical properties.

2. Characterization

a. Mechanical Test

Tensile strength measurement was carried out to determine the strength of the material against the tensile force. The tensile strength can be written mathematically as follows:

$$\sigma = \frac{F}{A} \quad (1)$$

where σ is the tensile strength (kg/cm^2), F is the tensile force (N), and A is the area of the sample (cm^2).

Strain is defined as a change in the size of an object due to the force in equilibrium compared to the original size. Strain in the composite was calculated using the following equation:

$$\varepsilon = \frac{\Delta l}{l} \quad (2)$$

where ε is the strain, Δl is the change in specimen length (cm), and l is the initial length of sample (cm).

Modulus of elasticity (E) is the ratio between stress (σ) and strain (ε). The modulus of elasticity is defined as:

$$E = \frac{\sigma}{\varepsilon} \quad (3)$$

b. Conductivity

Electrical conductivity is the ability of a material or material to conduct electric current. The conductivity of a conductor is greatly influenced by impurities or imperfections in the crystal. The value of the electrical conductivity of a material can be determined using the following equation:

$$\sigma = \frac{l}{RA} \quad (4)$$

where is the conductivity ($\Omega^{-1}.m^{-1}$) or (S/m), l is the thickness of the sample (m), R is the resistance of the material (Ω), and A is the cross-sectional area of the electrode (m^2).

c. Biodegradability Test

The simplest quantitative method for testing the biodegradation of a polymer is to determine the mass loss of material. The percentage of mass loss (ML) can be calculated using the following relation:

$$ML = \frac{m_i - m_f}{m_i} 100\% \quad (5)$$

where mi and mf are the mass of the specimen before and after the biodegradation process (g), respectively.

Degradability of a material can be determined from the rate of degraded mass at a certain time duration (Δt). Mathematically, degradability can be calculated using the following equation:

$$degradability = \frac{ML}{\Delta t} \quad (6)$$

d. Transparency Test

Plastic film transparency is defined as the transmission of visible light over a short distance at a wavelength of 540-560 nm. Visible spectrophotometer is a tool used to measure the transmittance and absorbance of a sample as a wave function in visible light. Visible light is light with a wavelength of 400-800 nm and an energy of 299-149 kJ/mol. The energy possessed by visible light can make electrons move from the ground state to a shell of an atom that has a higher energy called the excited state. The easier it is for the electrons to be excited, the greater the wavelength that is absorbed

e. Size Analyzer (PSA)

Particle size distribution after sonication for 2 h was measured with the Shimadzu SALD-2300 (WingSALD II-: Version 3.4.4). Particle size of cellulose samples in the form of colloids in water were measured using dynamic light scattering (DLS). A laser illuminated the samples and then the fluctuation resulting from the scattered light at various scattering angle was detected.

f. Fourier Transform Infrared Spectroscopy (FTIR)

The infrared spectrum in the range of 400 - 4000 cm^{-1} with a resolution of 4 cm^{-1} was recorded using Fourier transform infrared instrument (Thermo Nicolet, Avatar 370). FTIR spectrum of raw fiber and fiber treated with alkalis, hydrolyzed acid after milling and the bleached pulp was performed using attenuated total reflection (ATR) technique. The peak height was determined from the absorbance spectrum using the EZ OMNIC software.

RESULT AND DISCUSSION

1. Physical Properties of Nanofiber Composites

The tensile strength test was carried out using a Com Ten Testing Machine with a sample size in accordance with the ASTM D638-14 TYPE 5 standard. The test aimed to determine the effect of the addition of nanofibers on the tensile strength of the plastic film. Based on the results of measurements and calculations obtained data such as Figure 2.

The addition of areca nut nanofibers can increase the tensile strength of plastic films. The value of tensile strength continues to increase with the increase in the percentage of nanofibers, this is because nano-sized fibers will produce a large surface area, thereby reducing the number of cavities that make up bioplastics.

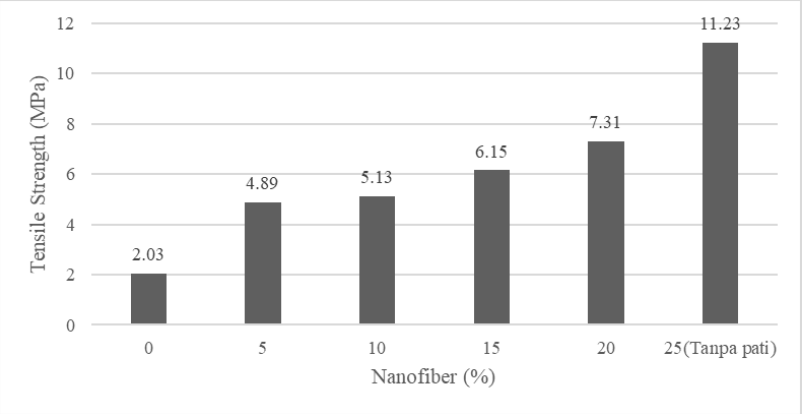

Figure 2. Graph of percentage of nanofibers with tensile strength.

Strain (elongation) testing was carried out to determine the effect of adding areca nut nanofibers on the ability of the plastic film to withstand the applied force before breaking. Based on the results of elongation measurements obtained data such as Figure 3. The highest strain value was found in the 25% nanofiber percentage, namely 55.17%. The addition of nanofibers as reinforcement can form hydrogen bonds due to the presence of hydroxyl groups. Nanofibers and starch can form a rigid network that can strengthen the plastic film.

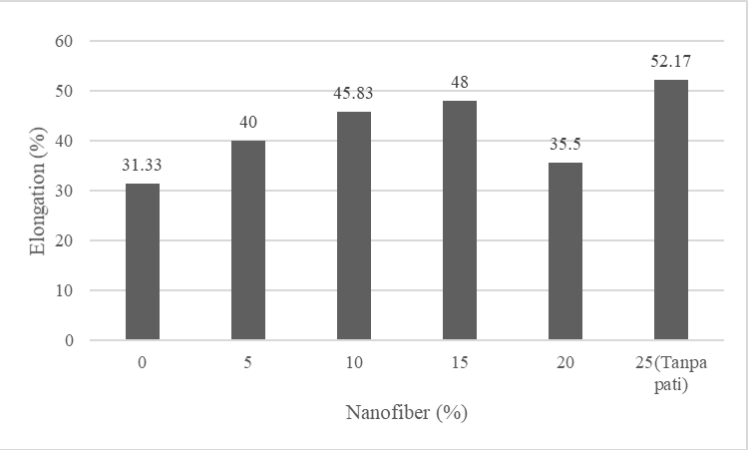

Figure 3. Graph of percentage of nanofibers with elongation.

The measurement of the modulus of elasticity aims to determine the ability of the plastic film to return to its initial shape after the applied force stops. Elasticity can be determined by comparing the tensile strength with the percent elongation. Based on the calculation results, the data is obtained as shown in Figure 4. The highest value of modulus of elasticity is 21.252 MPa on plastic films with the addition of 25% nanofiber percentage and the lowest is 6.479 MPa on plastic films without using nanofibers. This is because the more reactive nature of nanofibers causes the mobility of the polymer chain molecules to be higher.

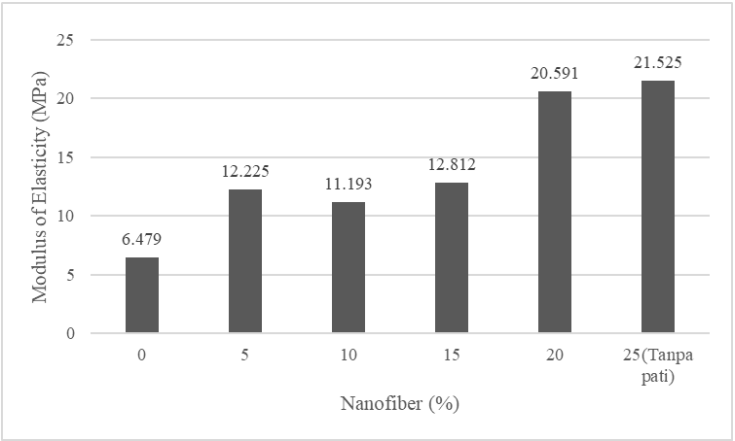

Figure 4. Graph of percentage of nanofibers with modulus of elasticity

2. Conductivity of Nanofiber Composites

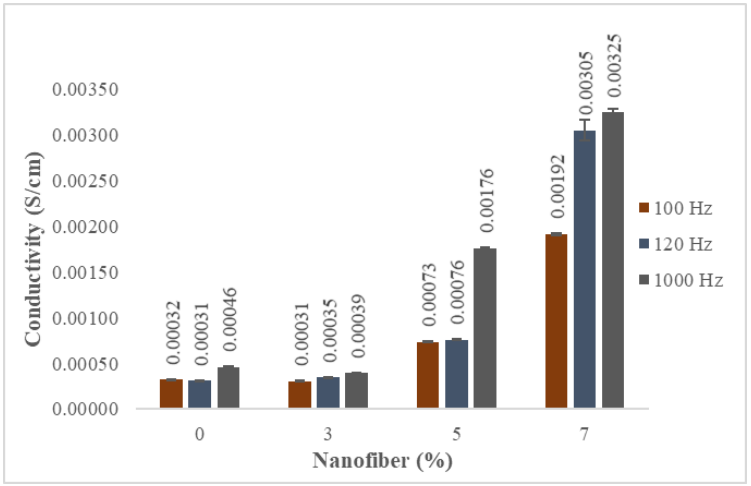

Figure 5. Graph of percentage of nanofibers with coductivity

Based on Figure 5, the conductivity value increases with the addition of the cellulose concentration. The highest conductivity value was found at 7% cellulose concentration, which was 0.00325 S/cm with a measurement frequency of 1000 Hz. The lowest conductivity value was found at 0% cellulose concentration, namely 0.00032 S/cm with a measurement frequency of 100 Hz. The conductivity value of nanocellulose composites is proportional to the magnitude of the given frequency. The higher the given frequency, the higher the conductivity value. The increase in frequency will increase the charge carriers on the material so that there is a high charge transfer in the interfacial area which results in increased conductivity.

3. Biodegradability of Nanofiber Composites

Biodegradation testing was carried out to determine the rate of change in the mass of the plastic film. The test was carried out by placing a plastic film on top of a container filled with soil. The initial mass of the plastic film was weighed and observed for 14 days. After 14 days the mass of the plastic was weighed as the final mass. Based on the results of measurements and calculations, the data is obtained as shown in Figure 6.

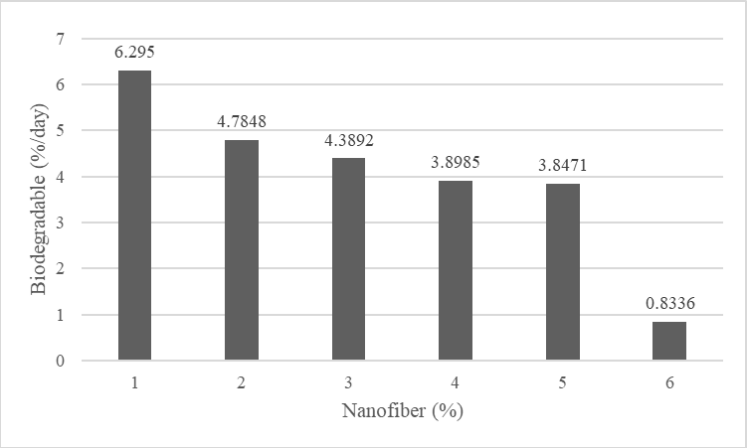

Figure 6. Graph of percentage of nanofibers with biodegradability

The resulting plastic film can be degraded by microorganisms in the soil with different percentages of mass loss according to the percentage of nanofibers contained in the plastic film. The higher the percentage of nanofibers, the lower the percent loss of biodegradation mass.

4. Transparency of Nanofiber Composites

Transparency test aims to determine the highest transmittance value that is passed on the plastic film. Based on the results of the plastic film transparency test, the data is obtained as shown in Figure 7.

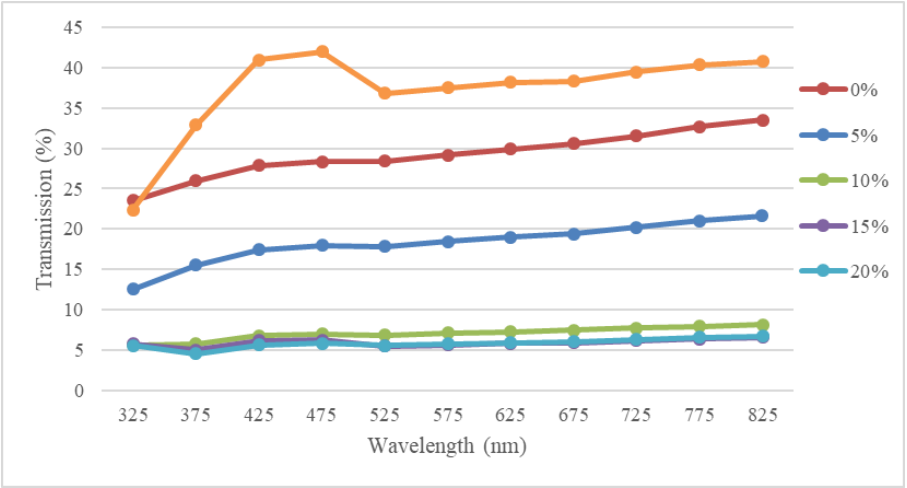

Figure 7. Graph of percentage of transmission with wavelength

Plastic film transparency is important in food packaging products because it will affect light-sensitive materials. Based on Figure 7, it can be observed that there is an effect of increasing the percentage of nanofibers on the transparency of the plastic film. The highest transmittance value was in the plastic film without using starch at a wavelength of 775 nm with a transmittance value of 40.36%. The lowest transmittance

value is at 20% fiber percentage at a wavelength of 775 with a transmittance value of 6.38%. It can be seen that the higher the percentage of nanofibers, the lower the transparency, meaning that the resulting plastic film is more opaque.

5. Particle Size of Nanofiber Composites

Colloid cellulose samples after 2 hours sonication were analyzed using Particle Size Analyzer (PSA). The size distribution of the nanocellulose fibrils is given in Figure 8. The data show that the cellulose is in the nanometer range with an average diameter of 75 nm and the small particle size distribution is visible. The graph shows the mode (most frequently occurring data) on the fiber diameter showing 72 nm. The Dynamic Light Scattering spectrum of nanocellulose suspensions from pineapple fibers also behaved similarly [34]. Homogenization plays an important role in obtaining nanocellulose dispersions with a narrow size distribution.

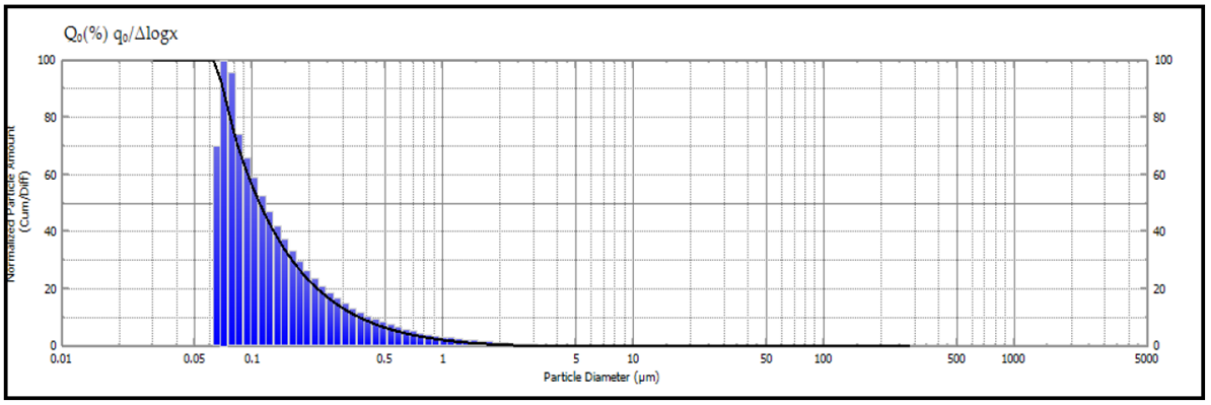

Figure 8. Particle size distribution from PSA measurement.

6. FTIR Spectroscopy of Nanofiber Composites

FTIR spectroscopy was performed to study changes in chemical structure after various fiber treatments. The FTIR spectrum of areca fiber, treated with hydrolyzed and bleached acid is shown in Figure 9. The FTIR spectrum shows the main cellulose uptake and the corresponding lignin functional groups. As previously discussed, areca fiber consists mainly of cellulose, hemicellulose, and lignin. Alkanes, esters, aromatics, ketones and alcohols, with different oxygen-containing functional groups are the main functional groups present in the samples. The loss of some peaks in the spectrum indicates the removal of some components after chemical treatment of the fiber.

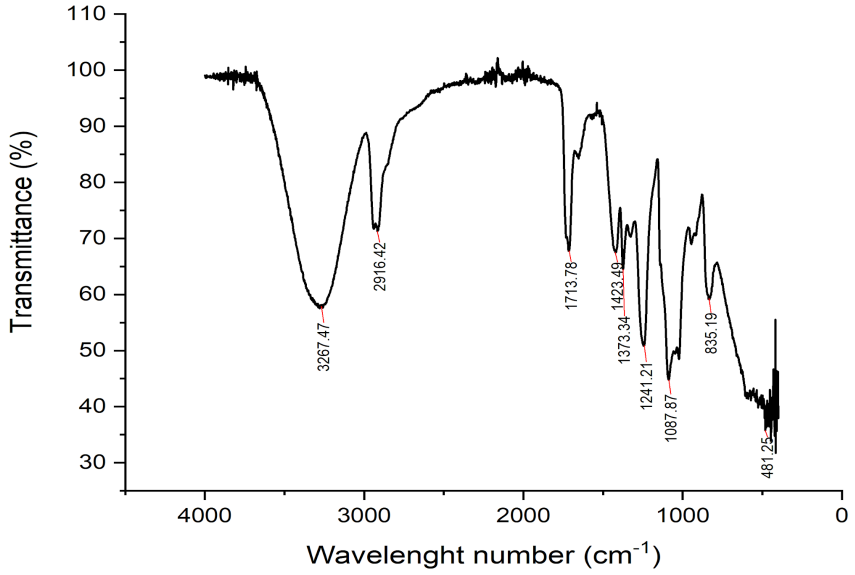

Figure 9. FTIR spectrum of nanofiber composites

Based on Figure 9, it can be seen that the results of the spectrum of the functional groups of the plastic film with a wave number range of 400-4000 cm^{-1} can be observed. The wave number 3267.47 cm^{-1} is related to the -OH (hydroxyl) group strain. This vibration peak indicates the absorption of water molecules in starch and nanocellulose. The widening of the peaks and the reduced intensity of the passed functional groups indicate that each component in the plastic film with its functional groups experienced a better interaction. At the peak of the wave number 2916.42 cm^{-1} is related to the vibration of the C-H group (alkane) which indicates the presence of cellulose in the plastic film. At the wave number 1713.78 cm^{-1} associated with the C=O (carbonyl) group. The peaks of wave numbers from 1423.49 cm^{-1}, 1373.34 cm^{-1} and 481.25 cm^{-1} indicate the presence of C-H group vibrations. The peak of the wave number 1241.21 cm^{-1} is related to the C-N (amine) group. The peaks of wave numbers 1087.87 cm^{-1} and 835.18 cm^{-1} are associated with the C-O (ester) group. The functional groups C=O and C-O are hydrophilic groups, namely the ability of the two groups to bind water molecules originating from the environment which causes microorganisms to decompose plastic. The presence of C=O and C-O groups in the synthesized plastic indicates that the plastic film has biodegradability [25,26]. The functional groups of the plastic film made from jackfruit seed starch are -OH, C-H, C=O, C-O.

CONCLUSION

Based on the results of the experiment, it can be concluded that areca nut fiber can be produced into cellulose through a combination of chemical and mechanical treatments. The thin film produced from nanocellulose with polyvinyl alcohol has a length of 7.5 cm with a width of 2.5 cm and a thickness of 0.05 mm. The highest conductivity value was produced by the nanocellulose concentration of 7% with a value

of 0.00325 S/cm. The conductivity value increased with increasing nanocellulose concentration and the conductivity value was proportional to the increase in measurement frequency. Nanofibers have a particle diameter of 79-187 nm with a particle distribution of 25%, 50% and 75%. The higher the percentage of nanofibers, the tensile strength and modulus of elasticity increase. Meanwhile, transparency and biodegradation are decreasing. There are functional groups C=O and C-O on the plastic film is a hydrophilic group which indicates that the plastic film can be degraded. The highest degradation was in the sample without using nanofiber, which was 88.13% for 14 days.

DECLARATION

All authors have contributed an equal amount of work to this article. All authors have read and agreed to the published version of the manuscript. Data available on request due to restrictions e.g. privacy or ethical: The data presented in this study are available on request from the corresponding author. The data are not publicly available due to avoid using the data for publication in other journals. Authors would like to thank Faculty of Mathematics and Natural Sciences Universitas Andalas for research funding. The author declares that there is no conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/or falsification, double publication and/or submission, and redundancies have been completely observed by the authors.

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