

Utilization of Cellulose from Pineapple Leaf Fibers as Nanofiller in Polyvinyl Alcohol-Based Film

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ABSTRACT

Cellulose from pineapple leaf fibers as one of the natural polymer which has biodegradable property in a nanometer's scale can be formed as a filler in the composite of Poly(vinyl) Alcohol/PVA is expected to increase the physical, thermal, and barrier properties of composite films similar to conventional plastic. The aim of this study was to examine the effect of fibrillation of cellulose fibers from pineapple leaf fibers using a combined technique of chemical-mechanical treatments and to investigate the reinforcing effect of concentration of nanocellulose fibrils in the polyvinyl alcohol (PVA) matrix. The effect of reinforcing on physical properties, thermal properties, water vapor transmission rate, light transmittance and morphological with and without the addition of glycerol were investigated. Nanocellulose was made from the cellulose of pineapple leaf fiber using wet milling (Ultra Fine Grinder). The composite film production was carried out by using casting solution method by mixing PVA solution with nanocellulose (10-50%) and glycerol (0-1%). The characterization of film covered physical properties (thickness, moisture content, and density), thermal properties, permeability (WVTR), light transmittance, morphology, and crystallinity. Nanocellulose from pineapple leaf fibers was produced by Ultra Fine Grinder shows that the size reduction process was accurate. Nanocellulose addition on PVA composite film was affected by increasing the physical, thermal, and barrier properties. Meanwhile, decreasing the percentage of composite film transmittance, thus the transparency decrease (opaque). Water vapor transmission rate (WVTR) the film was increased with increasing glycerol concentration, but the physical and thermal properties were decreased.

Keywords: nanocellulose; physical properties; thermal properties; barrier properties, glycerol

ABSTRAK

Selulosa serat daun nanas sebagai salah satu polimer alami dan bersifat biodegradable dalam ukuran nanometer dapat dijadikan sebagai filler dalam komposit Polivinil Alkohol (PVA) yang diharapkan mampu meningkatkan sifat fisik, termal dan sifat barrier film komposit yang setara plastik konvensional. Penelitian ini bertujuan untuk mempelajari pengaruh proses kimia-mekanis terhadap fibrilasi selulosa serat daun nanas, dan menyelidiki pengaruh penambahan nanoselulosa serat daun nanas terhadap peningkatan sifat fisik, termal, barrier (permeabilitas), dan tingkat transparansi film komposit. Nanoselulosa dibuat dari selulosa serat daun nanas menggunakan metode wet milling (Ultra Fine Grinder). Pembuatan film komposit dilakukan menggunakan metode casting solution larutan PVA dengan nanoselulosa (10-50%) dan gliserol (0% dan 1%). Karakterisasi meliputi sifat fisik (ketebalan, kadar air dan densitas), sifat termal, permeabilitas (WVTR), light transmittansi, morfologi dan kristalinitas. Proses pembuatan nanoselulosa serat daun nanas menggunakan Ultra Fine Grinder merupakan proses yang akurat. Penambahan nanoselulosa dalam film komposit PVA dapat meningkatkan sifat fisik, termal, dan barrier. Sedangkan persentase transmisi menurun sehingga transparansi film komposit buram. Penambahan gliserol yang semakin meningkat konsentrasinya telah meningkatkan WVTR, tetapi sifat termal dan fisiknya menurun.

Kata Kunci: nanoselulosa; sifat fisik; sifat termal; sifat barrier; gliserol

INTRODUCTION

Plastic is one of the chemical polymers that usually used as packing material on daily life. Even though

plastic has those advantages, a high dependence on plastic could make bad effect not only on human health but also for the environment. Due to that reason, there is an urgent need to find a new alternative packing

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material which is save for our body and environmentally friendly to replace plastic. On the other hand, environmental friendly packing material has some disadvantages mainly due to having lower mechanical stability.

A natural material with biodegradable properties such as plant's fiber can produce composite plastic that has excellent modulus elasticity [1]. Cellulose fiber is one of the natural polymers, which is adamant and relatively cheaper [2]. The used can be very straight forward by partially substituting expensive-oil derived plastic materials as in wood polymer composites [3-4] or natural fiber reinforced composites [5]. According to Kengkhetkit and Amornsakchai, compared to other natural fibers, pineapple leaf fibers exhibits superior properties [6]. The chemical composition of pineapple leaf fibers indicates a considerable potential as sources of cellulose that is α -cellulose with a composition of 98.63% [7]. The advantages of α -cellulose compared to other types of cellulose are having a long polymer chains, a high degree of polymerization and also the highest degree of purity and quality of cellulose [7]. The physical and mechanical properties of pineapple leaf fibers are relatively superior to that of cotton fibers and other natural fiber [8], thereby could be potentially developed as composite materials for reinforced plastic materials. The use of pineapple leaf fibers will not just to replace or substitute the expensive oil-derived plastic, but also to improve mechanical performances of the products [6]. In addition to its properties, use of pineapple leaf fibers in Indonesia would be relatively cheaper because the pineapple plant has been cultivated widely in Indonesia.

Recently, the new type of plastic has been developed through nanotechnology innovation. The long chain of cellulose molecules can be created in nanometer scale. Fibril from the cellulose fiber in nanometer scale has higher mechanical properties and huge interfacial area compared to whole fiber [9]. Therefore, composition with uniform distribution can change the molecule mobility and relaxation properties resulting in the composite which has flexibility, stiffness, and good heat characteristics and electrical isolator property [10-13]. Nanofibers from pineapple leaf are shown entanglements and branching with hygroscopic desired for food packaging applications, such as non-toxic, high hygroscopic, relatively inexpensive and abundantly available [14], high thermal stability (225 °C), high crystallinity (73%) [15].

Poly(vinyl) Alcohol/PVA is a synthetic polymer that easily soluble in water, slightly soluble in ethanol, but insoluble in other organic solvents, having no smell and taste, unpoisonous, and can degrade naturally [16]. PVA was combined with other polymer or filler, can increase the physical, thermal and barrier properties [17].

According to Roohani et al., PVA has an excellent compatibility with the addition of nanocellulose filler which produces environmental friendly nanocomposite [13].

Few research on composite film has shown that the addition of nanocellulose fibers can improve the physical properties [11,18-19], thermal properties [20], and barrier properties [21]. The physical properties can be increased by the addition of plasticizers, such as are mono and di-polyols, oligosaccharide, glycerol, and sorbitol. The type and concentration of plasticizer can affect physical properties and permeability of film in water vapor [22-23].

The aim of this study was to examine the effect of fibrillation of cellulose fibers from pineapple leaf fibers using a combined technique of chemical-mechanical treatments. Furthermore, the objective was to investigate the reinforcing effect of concentration of nanocellulose fibrils in the polyvinyl alcohol (PVA) matrix. The effect of reinforcing on physical properties, thermal properties, water vapor transmission rate, light transmittance and morphological with and without the addition of glycerol were studied. Earlier studies made on nanofibrils of pineapple leaf fibers as nanocomposite was prepared using Ultra-Fine Grinder, reinforced in a polyvinyl alcohol matrix particularly used for food packaging application especially for fruits has not been reported before.

EXPERIMENTAL SECTION

Materials

The research was conducted at Nanotechnology Laboratory of Indonesian Center for Agricultural Postharvest Research and Development (ICAPRD), Bogor, Indonesia, from June until December 2014. Materials used for research were Poly(vinyl) Alcohol/PVA (Celvo™ Sekisui Chemical Co. Ltd.), pineapple leaf fibers (CV. Hasanah Niaga, Bandung, West-Java), technical glycerol (Brataco PT.), distilled water and other materials for analysis.

Instrumentation

Instruments used were hot plate, teflon, Memmert oven, desiccators, Ultra-Fine Grinder (Matsuko Corp, Japan) and the testing instruments which were Particle Size Analyzer (Malvern), Perkin Elmer STA 6000 equipments, Scanning Electron Microscope (Zeiss EVO MA10), Transmission Electron Microscope/TEM (FEI Tecnai G2Spirit), X-ray Diffraction /XRD (Bruker D8 Advance), Spectroscopy Carry 60 UV-VI, and Mocon Permatran for water vapor permeability test.

Table 1. Formula of composite films

No.	Sample codes	Concentration		
		[PVA] (% w/v)	Nanocellulose (% w/w)	Glycerol (% w/w)
1	P10N10G0	90	10	0
2	P10N20G0	80	20	0
3	P10N30G0	70	30	0
4	P10N40G0	60	40	0
5	P10N50G0	50	50	0
6	P10N10G1	89	10	1
7	P10N20G1	79	20	1
8	P10N30G1	69	30	1
9	P10N40G1	59	40	1
10	P10N50G1	49	50	1

Procedure

Preparation of pineapple leaf nanocellulose fibers

Celluloses from pineapples leaf fibers were isolated with lignin removal method using sodium chloride. This process decreases the proportion of lignin so that cellulose can be easily degraded. Cellulose isolated from the previous step was then hydrolyzed with acid sulfate solution (64% w/w) while stirring at 45 °C for 60 to 90 min. The hydrolyzed process was stopped by the addition of cold water. Afterward, the cellulose suspension was washed with deionized water and separated using a centrifuge. The cellulose obtained was then dialyzed and sonicated for about 20 min to disperse the cellulose into water.

Pineapple nanocellulose fibers were prepared using Ultra-Fine Grinder. The isolated pineapple cellulose fibers were diluted with distilled water up to 2% concentration. The suspension was put into Ultra-Fine Grinder with 1500 rpm in various gap levels (respectively on gap 0, gap -3, gap -5 and gap -10). The process was repeated for 10-20 times until producing a bulky suspension. Nanocellulose fibers suspension was kept inside the refrigerator. The PSA instrument was used to see the size of nanocellulose particles on dilution of 10 times and refractive index average of 1.3365.

Preparation of PVA-nanocellulose composite films

PVA crystal (1.8 g) was diluted with distilled water (15 mL) and heated to 80 °C by using a hot plate for two h [21,24] until producing 10% (w/v) of PVA solution. Cool the solution until it reaches room temperature, followed by adding nanocellulose as much as 10, 20, 30, 40, and 50% (w/w). The plasticizer which was 1% of glycerol (w/w) can be added to the mixture and homogenized for 2 h. Composite film was formed by casting method using teflon (120 mm diameter) inside Memmert's oven at 65 °C for about 5 h. The composite film produced was placed into desiccator or closed container with silica gel inside. The formulas of composite film were shown in Table 1.

Characterization

Physical properties. The physical properties of the composite film characterized were thickness, water content and density. The film thickness measured by Mitutoyo 0-25 mm Micrometer with 0.01 mm precision by measuring 5 random spots from the sample. The films moisture content were determined according to the gravimetric method, after drying at 105 °C for 24 h and expressed in g water/g dry mass [25]. The film density was obtained by using the density equation, which is $\rho = \frac{m}{S \times \delta}$. Here, m is dry weight of the film (in g),

S is the surface area of the film (in cm²), δ is the film thickness (in cm), and ρ is the density of film (in g/cm³) [26]. The density of the sample film, which cut into 2 x 2 cm and placed for 20 days inside a desiccator, will be obtained by this formula.

Thermal properties. Simultaneous Thermal Analyzer (STA) was used to measure thermal transitions of PVA films and nanocomposite films. The test was performed with Perkin-Elmer STA 6000 equipment fitted with a gas Argon purged at 20 mL/min in accordance with ASTM E 967 [27] standard method. The samples were weighed (1-3 mg) in aluminum pans and a hermetically scale empty pan was used as a reference. All the measurements were performed in the temperature range of 30 °C to 480 °C at a heating rate of 10 °C/min.

X-ray Diffraction (XRD). XRD equipment is used for recording the film diffractogram in 25 °C. The X-ray source was Ni-filtered Cu K α radiation (40 kV and 35 mA). The composite films were mounted on a sample holder, and the pattern was recorded in the reflection mode at an angle 2 θ over a range of 5.000° to 80.009° at a speed of 5°/min.

Water Vapor Transmission Rate (WVTR). Observation on the permeability of composite film which covers Water Vapor Transmission Rate (WVTR), was measured by using Movon Permatran. Each sample was placed inside the desiccator in selected RH for 24 h. The size of film sample was 10 cm². The WVTR measurement followed the procedure of ASTM

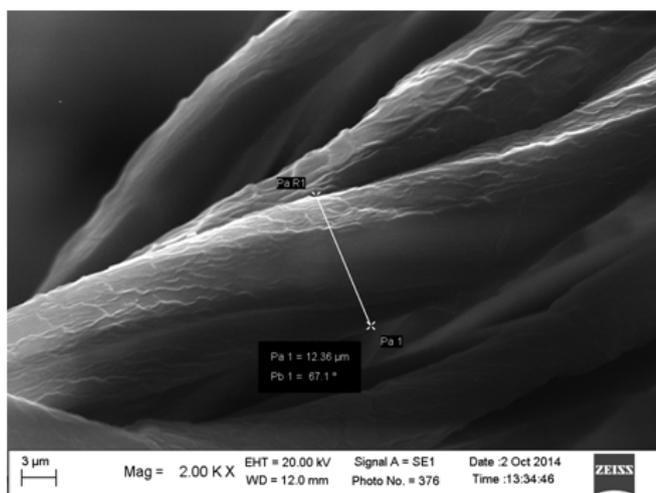


Fig 1. SEM images of pineapple leaf cellulose fibers at magnification 2,000X

E 96-93 [28] in which the upper flow configure to 10% RH while the bottom flow was 40-100% RH. The measurement was done in one hour until stable result values.

UV-Vis Spectrometer. Light transmittance of composite films was observed on UV-Vis spectrometer (Carry 60) in visible light wave-length range of 100-800 nm at 25 °C.

Scanning Electron Microscope (SEM). SEM analysis was carried out with the Zeiss EVO MA10 Scanning Electron Microscope. The small cut (2 mm x 2 mm) sample was fitted in cross section visualize bronze by using double-site tape. The surface of samples was coated with gold before imaging and observed with an accelerating voltage of 11.00 kv and the working distance (WD) of 11.5 mm.

Transmission Electron Microscope (TEM). The scatters of nanocellulose particles was observed using Transmission Electron Microscope (TEM) FEI Tecnai G2Spirit. Samples were diluted 20 times under operating conditions of the 120 kV high tensions using holey carbon grid.

RESULT AND DISCUSSION

Nanocellulose from pineapple leaf fibers was produced by a combination of chemical and mechanical treatments which aimed at delignification process and defibrillation process respectively. The morphology structures of cellulose of pineapple fibers obtained from the delignification process observed with SEM are presented at Fig. 1. It appears that not all of the cellulose fibers have broken down into small fibrils of cellulose. Most of the cellulose fibers are still united to form a bundle. This is caused by the present of lignin and hemicellulose which act as adhesive.

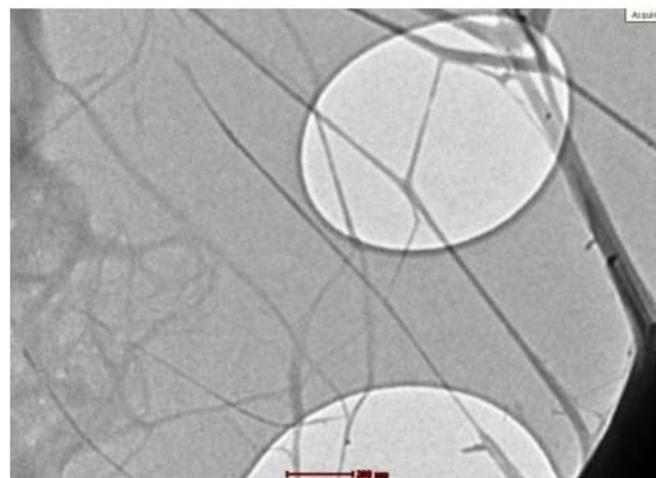


Fig 2. TEM images of pineapple nanocellulose fibers at magnification of 13,500X

The cellulose has to be treated mechanically with Ultra Fine Grinder to obtain the cellulose in the form of fibers (thread-like) and nanometer-sized. The particle size of nanocellulose fibers suspension obtained from the mechanical process was observed using Particle Size Analyzer (PSA) after dilution 10 times. Measurement result showed that pineapple nanocellulose fibers are having an average size of 284.6 nm. Observations of the internal structure of the nanocellulose by the use of TEM revealed that nanocellulose size was below 100 nm and already broken down into fibrils of cellulose, as shown in Fig. 2. This fact suggests that the size reduction process using Ultra Fine Grinder was accurate. Other techniques for steam explosion process coupled acid treatment [7] and high-pressure steam treatment [14] on the pineapple leaf fibers is found to be effective in the depolymerization and defibrillation of the fiber to produce nanofibrils of these fibers.

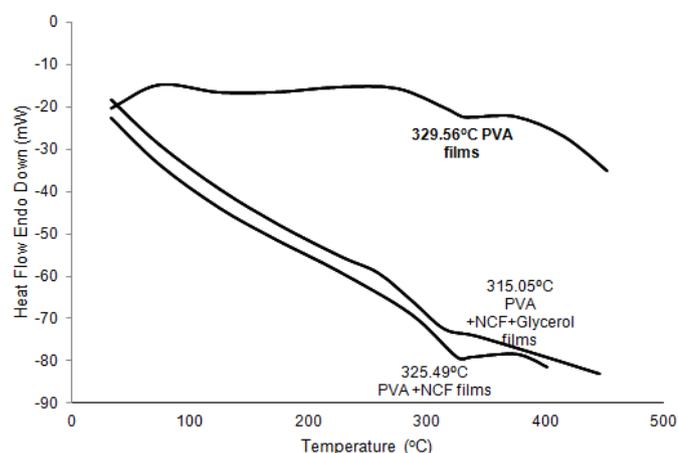
Thickness, Moisture Content and Density of Composite Films

The thickness value of the film can be seen on Table 2. It is shown that there was a change on the thickness of the film after significant addition of nanocellulose. The film became thinner for about 3–5 times before the nanocellulose addition (the thickness without nanocellulose was 0.11 ± 0.069 mm, while the thickness with nanocellulose was from 0.02 mm to 0.03 mm). This phenomena is happening due to hydrophilic PVA film, which is strong enough to bind water so that it affect the thickness. On the other hand, after the addition of nanocellulose, the film became thinner since the film from PVA and nanocellulose mixtures decrease this water-binding

Table 2. Thickness, density, moisture content, melting temperature and crystallinity of composite films with different concentrations of nanocellulose fibers

No.	Code of sample	Thickness (mm)	Density (g/cm ³)	Moisture content (%)	Melting Temperature T _m (°C)*	Crystallinity(%)*
1	NCF	0.14 ± 0.08	0.19 ± 0.05	2.34 ± 0.31	-	55.4
2	PVA (control)	0.11 ± 0.06	0.68 ± 0.01	6.03 ± 0.26	329.54	38.3
3	P10N10G0	0.03 ± 0.03	2.49 ± 0.15	2.92 ± 0.13	320.15	40.8
4	P10N20G0	0.03 ± 0.01	2.47 ± 0.39	4.27 ± 0.79	320.39	40.3
5	P10N30G0	0.03 ± 0.01	2.39 ± 0.02	4.58 ± 0.88	325.49	41.0
6	P10N40G0	0.02 ± 0.01	3.74 ± 0.02	2.53 ± 0.82	-	42.8
7	P10N50G0	0.02 ± 0.01	2.86 ± 0.13	3.98 ± 1.01	-	44.5
8	P10N10G1	0.03 ± 0.01	3.61 ± 0.63	7.71 ± 0.88	318.75	36.4
9	P10N20G1	0.03 ± 0.01	4.72 ± 1.49	6.03 ± 0.06	-	33.9
10	P10N30G1	0.03 ± 0.004	4.00 ± 0.78	5.51 ± 0.37	315.05	40.4
11	P10N40G1	0.02 ± 0.01	5.14 ± 1.62	5.62 ± 0.87	315.27	37.8
12	P10N50G1	0.02 ± 0.01	4.53 ± 0.96	5.49 ± 0.48	310.86	41.2

Remarks: * No statistical analysis involved because the test was only conducted one time

**Fig 3.** Heating scan STA curves of Control (PVA), and composite films

effect (hydrophilic properties decrease). The addition of nanocellulose 10–50% (w/w) is not significant to affect the change on thickness, which is only from 0.02 ± 0.014 mm until 0.03 ± 0.039 mm. This result is consistent with Müller et al. research which states that the addition of filler (cellulose fiber) in the biofilm is not too significantly to affect the thickness of the film [25].

One of the important physical properties is moisture content. The composite film with nanocellulose decreased the moisture content significantly up to twice compared to PVA film (Table 1). On the other hand, the addition of glycerol as plasticizer caused the increase of moisture content. This fact is due to hydrophilic properties of glycerol that can easily bind water. According to Rachtanapun and Tongdeesontorn, the addition of plasticizer increased hydrophilicity of films by exposing their hydroxyl groups [23]. Similarly, Mahmoud and Savello reported an increase of moisture content in

whey protein films as the glycerol concentration in the film formulation increased [29].

The nanocellulose addition also affected the density of the composite film. Table 2 show that the composite film density increased significantly from 4 to 8 times compared without the addition of nanocellulose. The density of film without glycerol addition raised around 4 to 5 times, while the density of the film with glycerol addition raised from 5 to 8 times than the density of PVA film. This fact was because the addition of glycerol to the composite film caused the hydrophilic of the film increased due to glycerol properties which are easy to bind water.

Thermal Analysis

The thermal properties of all-cellulose nanocomposite films were shown in Fig. 3 and Table 2. Guo et al. presented that the endothermic peak in heating was ascribed to the melting of association, aggregation and the hélix [30]. Melting temperature (T_m) of the all-cellulose nanocomposite films were presented in Table 2. As expected, T_m of PVA film (control) = 329.56 °C was higher than that of the all-nanocomposite films ($310.86 \text{ °C} < T_d < 325.49 \text{ °C}$). This could be ascribed to the lower homogenous as a result of blending between PVA matrix and nanocellulose. However, the addition of nanocellulose increased the T_m of nanocomposite films (Table 2). Sanchez-Garcia et al. reported that regarding higher loading, nano filler cellulose increased thermal stability [21].

Table 2 shows that the percentage of crystallinity of the composite films increased with the addition of nanocellulose up to 50% (w/w). This result was due to the nature of nanocellulose that has high crystalline properties i.e. 55.4%. An increase in the percentage of the composite film crystallinity caused T_m of composite

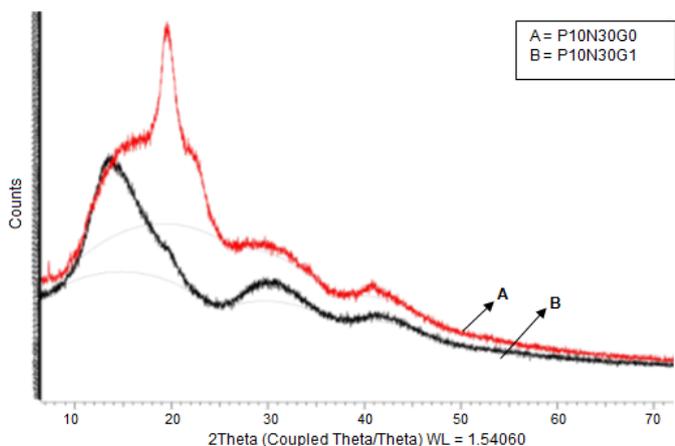


Fig 4. XRD patterns of composite films without glycerol addition (A), with glycerol addition (B)

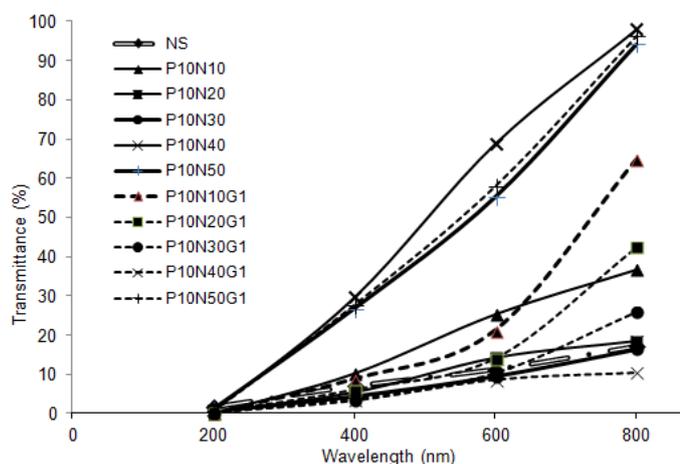


Fig 6. Light transmittance of composite films in the visible light wavelength range

the film also increased, but the addition of glycerol has lowered the value of the percentage crystallinity and T_m of the composite film. This fact was because the glycerol is a material capable of forming many hydrogen bonds and interacts with the polymer by interfering with a bond of the polymers thus creating a distance between the particles chain [31]. The disruption or unstable bonds between molecules in this composite film causing irregular spacing between molecules so that the interaction of attraction and weak bonds between the molecules of which shall mean the molecular are amorphous and percentage crystallinity of the film decreases. This result is also supported by the results of SEM composite film with the addition of glycerol in Fig. 7C, which is shown that the distribution of cellulose on the surface of the film is less obvious, which is suspected that a part of the hydrogen bonds in cellulose has been reacted with the hydroxyl group of glycerol, causing a series of crystal structure composed of an irregular form of non-crystalline or amorphous regions.

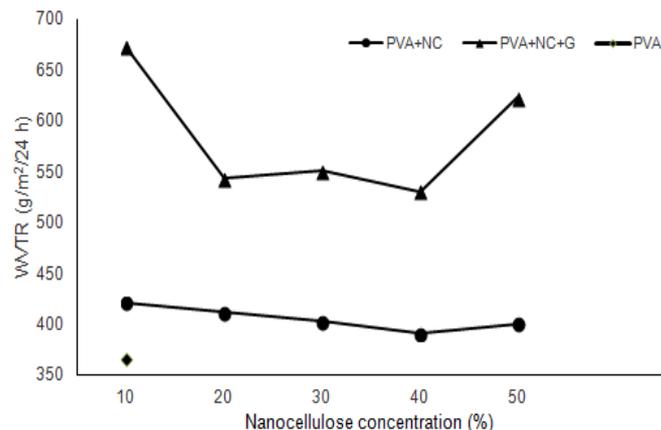


Fig 5. WVTR of PVA film (\diamond), PVA+Nanocellulose films (\bullet) and PVA+Nanocellulose+Glycerol films (\blacktriangle)

X-ray diffractogram also supports this fact; Fig. 4 shows the change in the intensity of the diffraction peaks in the composite film before and after the addition of glycerol. Fig. 4 indicates that film nanocomposite after glycerol addition is despite the low cellulose content, the peak is clearly visible. This result provides additional evidence that the original crystalline structure of cellulose is still present in the nanocomposite with glycerol addition. Most likely, nanofibril surfaces and disordered regions are swollen, without any influence on the interior of crystalline regions [14]. According to Chen et al. the changes in the intensity of the diffraction peaks indicated a change in the crystal structure or irregularity of the molecular chains of cellulose [32].

On Fig. 3 and Table 2 for P10N40G0, P10N50G0 and P10N20G1 films, it is interesting to note that the glass transition or melting temperature (T_m) is hardly detectable, indicating that, in these samples, the applied cooling conditions were not able to induce the complete PVA crystallization. This phenomenon is happening because of the surfactant influence, being able to interact with the polymer chains and affect its thermal properties and crystallization process [33].

Water Vapor Transmission Rate

Water Vapor Transmission Rate is one of the parameters used to determine the permeability of packaged goods. The lower the WVTR is the more resistance of the goods against water vapor or the more ability to resist the rate of water evaporation. According to Saxena and Ragauskas, crystalline nanocellulose with strong hydrogen bond group caused the correction of the WVTR value on composite nanocellulose polymer [34].

From Fig. 5, it is seen that the addition of nanocellulose can lower WVTR value, which means it

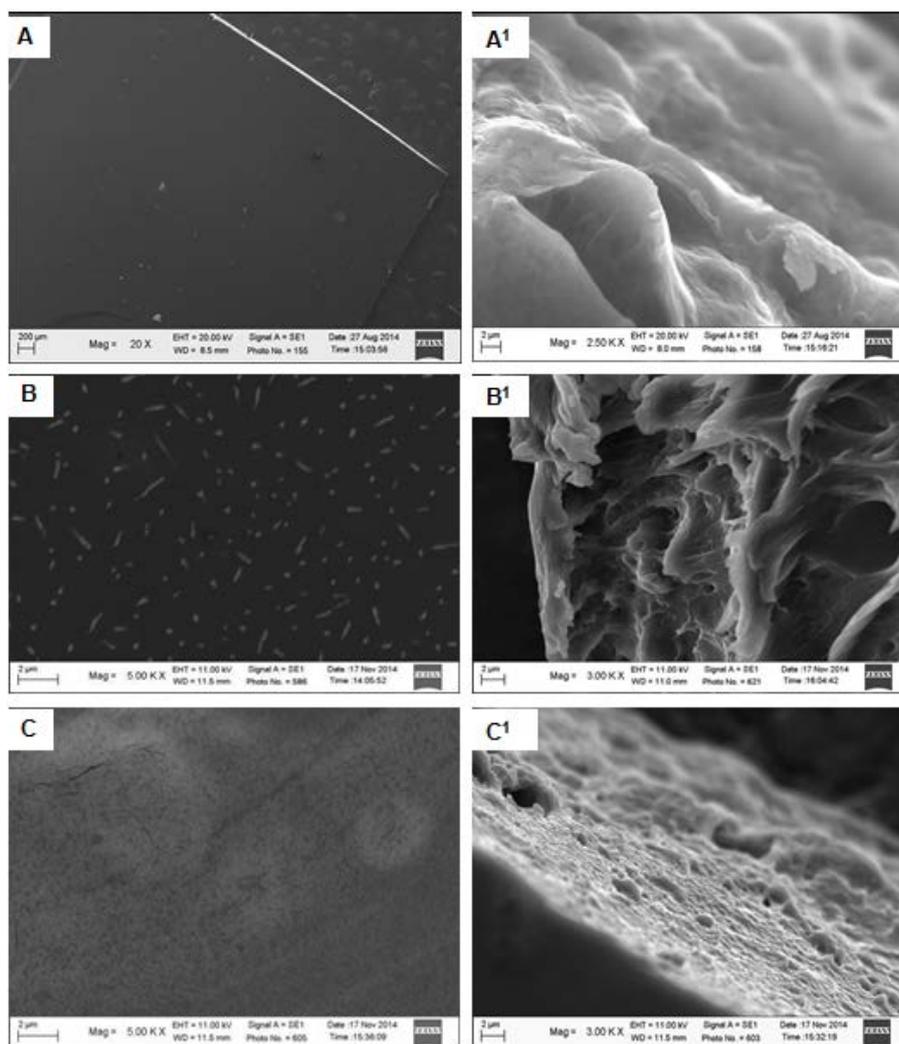


Fig 7. SEM images of film surface of PVA (A), PVA+Nanocellulose (B), PVA+Nanocellulose+Glycerol (C)

resist the transmission of water vapor. Experiment result of Pereda M et al. stated that permeability of nanocomposite film decrease with an increment of nanocellulose filler that added [21]. Similar to composite film without glycerol, the optimum concentration increase between 20-40% since if it is more than 40%, the WVTR value will increase again. This fact is caused by the lack of homogeneity of the nanocellulose into the mixture because the mixing process was carried out in the similar condition of reaction time and stirring speed for all types of treatment. Meanwhile, the plasticizer addition usually increases WVTR since plasticizer has hydrophilic properties that will stretch available hydrogen bond. Hence the vapor transfer from the environment to the surface of sample film will be faster. This fact will affect permeability with the raise of WVTR value compare with no glycerol addition. Based on Rachtanapun and Tongdeesoontorn, the plasticizer addition causes higher permeability of water vapor on film, water vapor

transmission rate (WVTR) increased with increasing glycerol concentration in film solution [23].

Light Transmittance of Composite Film

Fig. 6 showed that the nanocellulose film has low light transmittance (around 0.1%) and the observation on the transparency level of the film. On the surface, nanocellulose film from pineapple leaf fibers is not spread evenly, rough, and appears to be porous. This condition causes a high chance for vapor to interact with the surface of the film. Thus the light is not only reflected and refract by both surface film and vapor but also absorb toward the nanocellulose film. Hence, only a few of the light transmit into this film. PVA film is transparent with nearly 40% light transmittance at a wavelength of 800 nm (Fig. 6). However, after the nanocellulose addition into PVA, the light transmission significantly decreases. As the concentration of

nanocellulose addition increase, the light transmission of composite film decrease. Although the value of light transmission is low, the composite film still showed a good result. Tang et al. revealed that the Cellulose Nanofibrous Mats (CNM) shows very low visible light transmittance (7%), as demonstrated by the fact that letters under the CNM cannot be seen and with substantially increasing of CNMs in the composite film, light transmittance decreased [19]. The Glycerol addition on composite film does not affect much on the light transmission value. Fig. 6 showed that composite film with glycerol addition has a similar percentage of light transmission and transparency with the composite film without glycerol addition.

SEM Analysis

The observation of the structure of the surface morphology using SEM is shown in Fig. 7. Fig. 7 (A) which is a PVA film, seem not porous or flat, and Fig. 7 (B) shows that the composite films based on PVA-nanocellulose (pineapple leaf fibers) visible porous or flat structure have a surface morphology. The porous or flat that appear on the surface suspected that the nanocellulose unevenly distributed on the surface of PVA. An increasing concentration of nanocellulose affects the distribution on the surface of the PVA. By increasing the percentage of nanocellulose added caused the distribution of nanocellulose grows dense, so it will greatly affect the physical, thermal, barrier and the crystallinity of the film. Meanwhile, the addition of glycerol is also very influence to the surface of the composite film. Fig. 7 (C) shows that the distribution of nanocellulose on the surface is not visible, or suspected to have melted because part of the hydrogen bonds in cellulose has been reacted with the hydroxyl groups of glycerol, thus produced more smooth and flat film. Cherian et al. reported that a homogeneous distribution of the nanofibers in the polyurethane matrix was observed in the nanocomposite micrograph, implying excellent adhesion between fillers and matrix [14]. This result should be attributed to the hydrophilicity of both nanocellulose and polyvinyl alcohol and the hydrogen-bonding interactions existing in filler/filler and filler/matrix, where the hydroxyl ($-O-H$) group of nanocellulose and glycerol can interact with the carbonyl ($>CO$) group of the polyvinyl alcohol matrix. Thus an even and uniform distribution of the nanocellulose in the polyvinyl alcohol matrix is feasible.

CONCLUSION

Nanocellulose from pineapple leaf fibers was produced by a combination of chemical and mechanical treatments by Ultra Fine Grinder shows that the size

reduction process was accurate. Nanocellulose addition on PVA composite film was affected by increasing the physical, thermal, and barrier properties. Meanwhile, decreasing the percentage of composite film transmittance, thus the transparency decrease (opaque). Water vapor transmission rate (WVTR) the film was increased with increasing glycerol concentration, but the physical properties (moisture content and density) and thermal properties (melting point and crystallinity) were decreased.

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