Improved properties of corn starch-based bio-nanocomposite film with different types of plasticizers reinforced by nanocrystalline cellulose

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ABSTRACT
A single-use of the corn starch-based bionanocomposite film has several weaknesses, such as stiffness, ease of brittleness, and low moisture barrier properties. The addition of plasticizers and nanocrystalline cellulose (NCC) is expected to increase packaging properties. This study used corn starch var. Paragon from Indonesia as a raw material to produce the strong film. The study aimed to evaluate the physical and mechanical properties of the bionanocomposite film based on corn starch with the addition of different plasticizers (glycerol (MW = 92.094 g/mol)/sorbitol (MW = 182.17 g/mol)) and different concentrations of NCC (0, 3, 5 wt.%). The result showed that the sorbitol plasticized film reinforced by 5 wt.% NCC was the most effective to improve the properties with the thickness 0.256 mm; the color values L*, a*, and b* 97.43, −0.04, 1.85, respectively; the water vapor transmission rate (WVTR) 2.259 g/m² h; the water solubility 30.73%; tensile strength 4.69 MPa; elongation at break 56%; and young’s modulus 0.084 MPa. This treatment significantly reduced the film’s brittleness and water solubility while increasing its flexibility, tensile strength, elongation, young’s modulus, and resistance to water vapor transmission. Plasticizers more markedly affected the elongation properties of the films. However, NCC more significantly affected the tensile strength and WVTR films. In conclusion, this provides a great opportunity for the development of bionanocomposite films as biodegradable packaging in the future.

Introduction
Corn starch is mostly used packaging biomaterial, as it is cheap, abundant, and biodegradable. It contains hydrocolloid components, which can be used to form a film matrix. According to Mua and Jackson, starch granules are not soluble, but in the presence of water and heat, they could swell. Starch can be deformed into thermoplastic starch (TPS) under high temperature and shear in the presence of plasticizer. During the thermoplastic process, the water contained in the starch and plasticizer plays a very important role, because plasticizers can form hydrogen bonds with starch and replace strong interactions between hydroxyl groups in the starch molecule. However, that film still has several weaknesses in physical and mechanical properties. The latest technology developed to improve this weakness by the addition of nanoparticles to the film. The formation of the nanocomposite film structure is strongly influenced by the interaction between the starch matrix, plasticizer, and the surface of the nanofiller. The plasticizer is suspected to be involved in the interaction between starch and nanofiller, which will affect the physical, mechanical, and moisture...
barrier properties. In this study, corn starch has an amyllose content of 29.96% and amyllopectin content of 44.02%, so the addition of an appropriate plasticizer and nanofiller can produce a strong and not easily broken film.\textsuperscript{[5]}

Nanocrystalline cellulose (NCC) is the organic nanoparticles that can be used as fillers in the nanocomposite film matrix. It is a derivative of cellulose obtained through mechanical digestion or acid hydrolysis. In the nanoform, the properties of cellulose molecules can be optimized. NCC has a large and reactive surface area, so it could provide good dispersion in the matrix.\textsuperscript{[6,7]} The accessible hydroxyl groups on the surface of the cellulose nanocrystals will interact with the hydroxyl groups of the plasticizers, changing the morphology and imparting new properties. Even at low concentrations, cellulose crystallites have a remarkable reinforcing effect when homogeneously dispersed in polymer matrices.\textsuperscript{[8]}

Unfortunately, starch-based bionanocomposite films reinforced by NCC only are often stiff and brittle so plasticizers are necessary to increase the properties when the film is pulled. Plasticizers are low molecular weight substances that are incorporated into the polymer matrix to increase the flexibility and processability of the film. Polyols such as sorbitol and glycerol are good enough plasticizers to reduce internal hydrogen bonds in order to increase the intermolecular distance.\textsuperscript{[9]} They can decrease the intermolecular strength, increase flexibility and extensibility so that a film with good mechanical quality is produced.\textsuperscript{[10,11]} Besides, both of them can inhibit the evaporation of water from the substance by reducing internal hydrogen bonds in intermolecular bonds, and they can dissolve in each polymer chain to promote the movement of polymer molecules on the film. Both polyols have a similar molecular structure, but they have different effects on the properties of the starch film.

Several studies have reported the effect of the incorporation of NCC in the film matrix such as Eucommia ulmoides gum,\textsuperscript{[7]} pectin,\textsuperscript{[11]} starch-PVA,\textsuperscript{[12]} corn starch-gelatin,\textsuperscript{[13]} who found that it could increase the tensile strength and elongation at break and decrease the water vapor permeability (WVP). Several studies have reported on the effect of glycerol in the film matrix such as cassava-mung bean starch\textsuperscript{[14]} and corn starch,\textsuperscript{[15]} who reported that it could reduce the brittleness and increase the flexibility of the film. Moreover, recent studies have indicated the effect of sorbitol in the film matrix such as maize starch,\textsuperscript{[8]} cotton CNC film and flax CNC film,\textsuperscript{[16]} PVA-chitosan,\textsuperscript{[17]} who investigated that it could

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1}
\caption{The appearance of glycerol plasticized film with 0% NCC (a), 3% NCC (b), 5% NCC (c), and sorbitol plasticized film with 0% NCC (d), 3% NCC (e), 5% NCC (f) (images capture by a digital camera).}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2}
\caption{SEM of the surface and cross-section of glycerol plasticized film with 0% NCC (a,g), 3% NCC (b,h), 5% NCC (c,i), and sorbitol plasticized film with 0% NCC (d,j), 3% NCC (e,k), 5% NCC (f,l).}
\end{figure}
Figure 3. FTIR spectra of bionanocomposite film.
increase thickness and flexibility of the film. Based on the studies mentioned above, the addition of different types of plasticizers, the concentration of NCC, and varieties of the corn could improve the physical, mechanical, and barrier properties of nanocomposite film.

To the best of our knowledge, there is limited information about the properties of bionanocomposite film based on corn starch with the addition of plasticizer reinforced by NCC. Hence, this study aims to investigate the role and the plasticizing effect of glycerol and sorbitol 2% (v/v) with different molecular weights and different concentrations of NCC (0, 3, and 5 wt.%) in the corn starch-based film matrix var. Paragon from Indonesia, and to obtain the most effective treatment in improving the properties of bionanocomposite film.

Materials and methods

Materials

Corn kernels var. Paragon was obtained from a local farmer (Sumedang, Indonesia). NCC of 413 nm (milled Microcrystalline Cellulose Vivapur MCG 811 F, Germany, ball milling process was carried out at PRINT-G Unpad). Glycerol (MW = 92.094 g/mol), sorbitol (MW = 182.17 g/mol), carboxymethyl cellulose (CMC) (Blanose France brand), filter paper (whatman no. 40), PP plastic (Bangkuang brand), silica gel (Wonder Natural brand) was obtained from Bratachem, Indonesia.

Starch extraction

The extraction of starch was determined by Marichelvam et al.[18] with slight modification. 500 g of corn kernels were added to 500 ml of water and then milled with a blender. The extraction of starch was carried out by filtration while adding 3000 ml of water, and the remaining residues were removed. The starch suspension was precipitated for 24 h, then centrifuged for 15 min at 4000 rpm to separate the wet starch and the filtrate. The wet starch had been dried in the oven at 50°C for 12 h. The dry starch was crushed with a grinder. The sieving was carried out with an 80 mesh sieve to obtain starch of a homogeneous and fine size.

Amylose and amylopectin analysis

Amylose and amylopectin were analyzed according to Subroto et al.[19] Amylose content analysis was carried out using the UV-Vis spectrophotometry method, while amylopectin content was measured by the difference method, which was determined from the difference between starch content and amylose content, while starch content was measured using the Luff-Schoorl method.

Preparation of bionanocomposite film

In this study, bionanocomposite film was made according to Kaushik and Kaur[8] with slight modification. 7 g of corn starch was mixed with 200 ml of distilled water to produce a 3.5% (w/v) corn starch solution. CMC (0.5% w/v) was added to the corn solution gradually while stirring continuously. After the CMC dissolved, the dispersed NCC (0, 3 or 5 wt.%) was added. Then the mixture was stirred and heated in a beaker glass that has been inserted with a magnetic bar while stirring on a hot plate stirrer. After the pasting temperature of corn starch gelatinization (62°C) was reached, 2% (v/v) of glycerol or sorbitol was added respectively. The film solution was stirred up to 70°C. Then, the solution was cooled to a temperature of about 40°C. The forming process was conducted by pouring the film solution into the film plate amount 0.42 g/cm². The film plates were placed in the oven at 50°C for 24 h.
**Bionanocomposite film color**

The color was measured using Spectrophotometer CM 5 (Konica Minolta Co., Osaka, Japan) with Spectra Magic software. The color measurement includes L* (lightness, 0 = black/100 = white), a* (+a* = redness/-a* = greenness), b* (+b* = yellowness/-b* = blueness) and hue. The calibration was performed with a zero-calibration plate (CM-A124) and white calibration plate (CM-A120) with a large target mask (CM-A203). The measurement was conducted by placing the film on the transmittance specimen holder and then shooting rays at two different parts.\(^{[20]}\)

**Bionanocomposite film thickness**

The thickness was measured using a micrometer screw at 5 different regions. Measurements were taken at the four corners and in the center of the film. Average values of five measurements were calculated in different regions of each sample.\(^{[21]}\) The thickness was stated in mm and the micrometer screw used has an accuracy of 0.01 mm.

**Water vapor transmission rate (WVTR)**

The water vapor transmission rate was analyzed according to Slavutsky and Bertuzzi.\(^{[22]}\) The film sample that would be tested was closed in a cup containing 10 g of silica gel (RH = 0%). Then the cups were subsequently placed in a jar containing 40% (w/v) of saturated NaCl salt solution (RH = 75%) at 25°C. The weight of the cups was measured every hour for 8 h, and weight loss from each cup was measured. Water vapor transmission rate (WVTR) was calculated from the slopes (linear) of the steady-state portion of weight loss of the cup versus time curve. Therefore, the slope of the linear line was calculated as water vapor absorption per hour (g/h). WVTR was calculated as follows:

\[
\text{WVTR} = \frac{slope}{A} \quad (1)
\]

where WVTR = water vapor transmission rate (g/m².h), slope = absorption of moisture every hour (g/h), A = film area (m²)

**Bionanocomposite film of water solubility**

Solubility was analyzed according to Atef et al.\(^{[23]}\) The cut samples in rectangular (a) and filter paper (b) were inserted into distilled water. After 24 h agitation (250 rpm) in 50 mL distilled water at 25°C, the samples were filtered through filter paper. Then, the filter paper dried at 105°C for 24 h to achieve the final dry weight (c), and the film solubility (%) was calculated using the equation:

\[
\text{Percent of solubility} = \frac{a - (c - b)}{a} \times 100\% \quad (2)
\]

where a = initial sample weight (g), b = filter paper weight (g), c = dry weight of filter paper and samples (g)

**Mechanical properties of bionanocomposite film**

Mechanical characteristic testing referred to ASTM.\(^{[24]}\) The tool used by the Universal Testing Machine Brand SHIMADZU AG IS, Japan, with a load cell 1kN and a speed of 10 mm/min. Before testing, the films were conditioned in room at 23°C at 50% RH for more than 40 hours. The tensile strength values, elongation, and young modulus were measured using the following formula:
\[
\sigma = \frac{F}{A}
\]  
(3)
\[
\varepsilon = \frac{\Delta l}{L} \times 100\%
\]  
(4)
\[
E = \frac{\sigma}{\varepsilon}
\]  
(5)

where \( \sigma \) = tensile strength (MPa, psi), \( F \) = Force applied to the material (N, lb), \( A \) = Area (cm\(^2\), in\(^2\)), \( \varepsilon \) = Stretch/Elongation (%), \( \Delta l \) = Change in elongation (cm), \( L \) = Initial length (cm), and \( E \) = modulus of elasticity (MPa, psi)

**Scanning Electron Microscope (SEM)**

The morphology film was analyzed using ScanningElectron Microscope JEOL JSM-6360LA (Japan). A thin film was frozen in liquid nitrogen, then fractured, mounted in a special holder, coated with gold, and examined. While analyzed the cross-section the sample was folded at 90° for inspection \[^{[8]}\].

**ATR-FTIR Spectroscopy**

The film spectrum was recorded in reflection mode using an FTIR spectrophotometer (Thermo Scientific® Nicolet iS5 with detector DGTS (Deuterated Triglyceride Sulfate), ZnSe iD3 ATR Holder (Total Attenuated reflection). A thin film was placed on the surface of the FTIR holder and the wave absorption was measured \[^{[17]}\].

**Statistical analysis**

The data were analyzed by univariate Analysis of Variance (ANOVA) using SPSS 19.0 Statistical Software Program to compare plasticizers and NCC concentrations in nanocomposite film and submitted to the mean comparison test by Duncan, at a significance level of 5% (\( P < .05 \)) to determine the significant difference between treatments.

**Results and discussion**

**Film thickness**

The thickness of bionanocomposite film is presented in Table 1. Based on JIS Standard,\[^{[25]}\] plastic film for food packaging had a maximum thickness of 0.25 mm. Generally, the thickness of the glycerol plasticized film was significantly higher than sorbitol regardless of NCC concentration was incorporated. This was caused by variations in the plasticizer’s ability to absorb water as well as the total solids produced. According to Mathew and Dufresne\[^{[26]}\] plasticizers with low molecular weight compounds had higher hydrophilic properties. Plasticizers with a low molecular weight had a greater number of

| Treatments   | Thickness (mm) | Water solubility (%) | WVTR (g/m\(^2\).hour) |
|--------------|----------------|----------------------|------------------------|
| G + 0% NCC  | 0.260 ± 0.005 \(^c\) | 36.843 ± 0.400 \(^d\) | 9.637 ± 0.222 \(^c\)   |
| G + 3% NCC  | 0.275 ± 0.005 \(^d\) | 34.125 ± 0.419 \(^c\) | 7.687 ± 0.321 \(^bc\)  |
| G + 5% NCC  | 0.281 ± 0.005 \(^d\) | 34.023 ± 0.391 \(^c\) | 6.960 ± 0.101 \(^b\)   |
| S + 0% NCC  | 0.181 ± 0.001 \(^a\) | 32.117 ± 0.305 \(^b\) | 8.237 ± 2.207\(^ac\)  |
| S + 3% NCC  | 0.205 ± 0.004 \(^b\) | 32.817 ± 0.050 \(^b\) | 3.715 ± 0.002 \(^a\)   |
| S + 5% NCC  | 0.256 ± 0.006 \(^c\) | 30.728 ± 0.503 \(^d\) | 2.259 ± 0.093 \(^a\)   |

The mean value of treatment denoted by the same letter indicates no significant difference at the 5% test level according to the Duncan test

G = Glycerol; S = Sorbitol; NCC = Nanocrystalline cellulose
final hydroxyl groups that were easily accessible to water due to their chemical structure. Because glycerol had a lower molecular weight (92.094 g/mol) than sorbitol (182.17 g/mol), more water was bound and increase the film thickness. This was consistent with Sitompul and Zubaidah,\(^{27}\) who stated that the more water was bound, the thicker the film would be. Observation showed that the moisture content of the glycerol plasticized film with 0%, 3%, and 5% NCC were 17.81%, 13.15%, and 10.49% respectively, while the moisture content of the sorbitol plasticized film with 0%, 3%, and 5% NCC were 9.22%, 8.27%, and 7.35% respectively, indicating that glycerol had a higher water content than sorbitol.

Furthermore, the thickness of the film tends to increase as the concentration of NCC increases. This was presumably because NCC could be acting as a good filler. Chaichi et al.\(^{11}\) explained that nanoparticles had a large surface area and energy to build strong interactions with the matrix and could be well dispersed in the matrix. The treatment of 5% NCC in sorbitol plasticized film was the significantly highest thickness of the 0% and 3% NCC in the same plasticizer. This was owing to the increasing of NCC concentration causing an increase in the total solids dissolved so that the viscosity of the film solution increases and finally the film thickness increases.\(^{28}\) Observation on viscosity, it was found that the viscosities of film solutions of glycerol or sorbitol plasticized film with 0%, 3%, and 5% NCC among 48 - 49 mPas, where NCC with high concentration increased the film solution viscosity.

**Film color and transparency**

The L*, a*, b* color values of bionanocomposite film by Chromameter are shown in Table 2. While the appearance of the film can be seen in Figure 1. Overall, all the L* values of the treatments were not significantly different. In this study, the film tended to have a high level of brightness because it was close to 100 values. The brightness was influenced by the ingredients added to the film-forming solution.\(^{10}\) In addition, there was a relationship between film thickness and brightness, where films with higher NCC concentrations will increase the total dissolved solids in the film solution, causing the film to grow thicker and could reduce light diffusion. This was in agreement with Sitompul and Zubaedah,\(^{27}\) who found that increasing the thickness of the film would decrease the transmitted light so that the brightness of the light decreased, and vice versa.

Based on Table 2, all of the films were obtained that a color of a* value did not tend to be greeness, due to it being a small value. The films had a slightly yellowish-white color. The glycerol plasticized film was significantly higher than sorbitol plasticized film regardless of NCC concentration was added. Amongst the treatments, sorbitol plasticized film with 5% NCC had the lowest a* value significantly. This was closely related to the addition of NCC, which had a white color, so as the NCC concentration increased, the green color (a*) decreased.

### Table 2. The L*, a*, b* value of bionanocomposite film.

| Treatments | L*    | a*    | b*    | Color image the films |
|------------|-------|-------|-------|-----------------------|
| G + 0% NCC | 97.69 ± 0.21 a | 0.30 ± 0.06 d | 3.54 ± 0.04 d | |
| G + 3% NCC | 98.06 ± 0.13 a | 0.46 ± 0.01 e | 2.32 ± 0.04 b | |
| G + 5% NCC | 97.63 ± 0.68 a | 0.24 ± 0.04 td | 2.92 ± 0.28 c | |
| S + 0% NCC | 98.49 ± 0.40 a | 0.19 ± 0.05 f | 1.66 ± 0.01 a | |
| S + 3% NCC | 97.62 ± 0.25 a | 0.09 ± 0.01 b | 1.78 ± 0.04 a | |
| S + 5% NCC | 97.43 ± 0.01 a | -0.04 ± 0.01 a | 1.85 ± 0.08 b | |

The mean value of treatment denoted by the same letter indicates no significant difference at the 5% test level according to the Duncan test.

G = Glycerol; S = Sorbitol; NCC = Nanocrystalline cellulose
L* = chromatic brightness; a* = chromatic green-red color; b* = chromatic blue-yellow color
Meanwhile, generally, the color of the b* value was tended to be yellowish. This might due to the xanthophyll pigment found in corn kernels naturally. Also, it could be caused by heating, some of the oxygen atoms were lost from the crystal lattice then in this state produces a different color. Furthermore, the b* value of the glycerol plasticized film was significantly higher than sorbitol regardless of any concentration of NCC used. Glycerol was presumed to have a greater impact on the formation of b* color values on the starch-NCC film than sorbitol. Furthermore, the glycerol plasticized film was not significantly different at each concentration of NCC, however, the glycerol plasticized film was significantly different at each concentration of NCC. This was also due to the effect of the NCC white color which significantly reduced the yellowness (b*) of the film.

**Film water solubility**

The water solubility of bionanocomposite film is presented in Table 1. Generally, the percent solubility of glycerol plasticized film was significantly higher than sorbitol plasticized film at each NCC concentration were added. This might be caused glycerol had a lower molecular weight than sorbitol, which could easily interact with starch-NCC polymer chains, resulting in increased water affinity. Furthermore, this was closely related to the plasticizer hydrophilic properties of glycerol, which were greater than sorbitol and could increase the film water solubility. This was consistent with Farhan and Hani, which found that glycerol plasticized film had a higher water solubility than sorbitol.

Furthermore, the results showed that the incorporation of NCC could reduce the water solubility of the bionanocomposite films. The film with 0% NCC had the significantly highest solubility due to consisting of corn starch, CMC, and glycerol/sorbitol which were hydrophilic without the hydrophobic nanoparticles. Meanwhile, the film with 5% NCC had a significantly lower solubility due to the nanoparticles having regulated the strong hydrogen bonds between the nanoparticle’s hydroxyl groups with the hydroxyl and carboxyl groups in the polymer matrix. This could increase the interaction between molecules for increasing the cohesiveness of the polymer matrix. Moreover, the incorporation of nanoparticles caused the free water molecules to not strong enough to break the nanofiller-matrix bonds. Strong hydrogen bond networks with a polymer matrix and high film crystallinity were responsible for increasing water resistance. The increasing concentration of NCC caused the solution molecules and the film matrix to increase so that the film structure became more compact and stronger, as a result, the film was not easily leached by water. This was in line with Atef et al. explained that the increase of NCC concentration effectively increased the formation of hydrogen bonds between the polymer matrix and NCC in which NCC could increase the cohesiveness between the polymer-filler structure and so that increased water resistance.

**Water vapor transmission rate (WVTR)**

The water vapor transmission rate of bionanocomposite film is shown in Table 1, overall, the WVTR of glycerol plasticized film was significantly higher than sorbitol regardless the concentration of NCC used. This was thought to be closely related to the high hydrophilicity properties of the glycerol molecule so that it supported the adsorption of water molecules and contribute to the increase in film water vapor permeability. The presence of glycerol molecules between the polymer chains changed the structure of the polymer network, increasing the distance between the chains and thus increasing the diffusivity of water vapor through the film and thus accelerating water vapor transmission. Wittaya reported that the hydrophilicity of the plasticizers would increase the water content of the films, consequently increasing the mobility of the molecules and affecting permeate solubility in the films.

Meanwhile, sorbitol plasticized film was more effective in reducing WVTR than glycerol plasticized film at each NCC concentration. This value complied with the JIS standard as it was below 10 g/m² h. This was presumably because sorbitol could form a more stable hydrogen bond with starch and facilitate stronger interactions between the starch matrix and the NCC surface. In other words, the use of sorbitol could improve the balance of interactions between starch, plasticizer, and NCC, as well as
allowing more of the plasticizer and starch to diffuse together in the film. Sorbitol was assumed can serve as a better bridge between the starch and the NCC surface than glycerol so that more polymer enters the NCC surface leading to a decrease in the WVP value.

Furthermore, the increasing of the NCC concentration led to a decrease of WVTR value. This was due to the nanometer scale caused the movement of water on the film matrix to be difficult because the formation of a long winding path. The WVTR of sorbitol plasticized film with 3% and 5% NCC were significantly lower than the others. It occurred because the higher of NCC concentration, the more increased the formation of tortuosity structure in the film. Moreover, the formation of a hydrogen bond network between the NCC and the starch matrix in the film, which could prevent the formation of pores as water vapor pathways. Besides that, similar results were reported by Santana et al.,[3] who found the lowest WVP occurred for a cellulose nanofiber concentration of 3.44% and Huq et al.,[6] who found a significant decrease of WVP was obtained due to the incorporation of 5% NCC. They found that the crystalline domains with a high orientation degree that form when these nanoparticles were evenly distributed throughout the polymer matrix and acted as a labyrinth, preventing water vapor diffusion through the matrix by increasing tortuosity and length of the diffusion pathway.

**Mechanical properties**

Preliminary work demonstrated that corn starch-NCC films without plasticizer as relatively brittle and easily broken and needed to be handled very carefully. Hence, in this study, the mechanical properties of films were improved by using sorbitol/glycerol plasticizers and NCC at different concentrations. The mechanical properties of films were influenced by the composition and the concentration of the materials used in their preparation. Amylose had affected the compactness of the structure and strength, amyllopectin had a role in the elasticity and clear color, NCC would help to improve the physical properties, while glycerol/sorbitol affected the increasing elongation, reducing stiffness and brittleness of the film.[15]

The tensile strength, elongation, and young’s modulus bionanocomposite films are shown in Table 3. Overall, the tensile strength of the sorbitol plasticized films was significantly higher than the glycerol plasticized films at all NCC concentrations by 4.11 MPa, 3.17 MPa, and 4.69 MPa, respectively. This was fulfilled with the standards by JIS[25] which was minimum of 0.392 MPa. This was presumably because the molecular weight of sorbitol was higher than glycerol. When the molecular weight of the plasticizer increased, the number of plasticizer molecules interacting with the amyllopectin chains decreased, and the plasticizing effect was lower for the same plasticizer content.[16] Also, this was in line with Mathew and Dufresne,[26] who found the films had high mechanical properties, such as stiffness and elongation at break could be obtained with high molecular weight plasticizers (i.e. with sorbitol).

Deeply, increasing NCC concentration resulted in an increase in tensile strength film. The sorbitol with 5% NCC was the significantly highest tensile strength from the others, which increased by 14.19 fold. This was influenced by the integration of NCC into the starch matrix, strong interactions between cellulose crystallites and starch matrix occur, limiting starch matrix chain motion. Huq et al.[6] reported that the addition of 5% NCC could be well dispersed in the nanocomposite film matrix effectively

| Treatments | Tensile strength (MPa) | Elongation at break (%) | Young’s Modulus (MPa) |
|------------|------------------------|-------------------------|-----------------------|
| G + 0% NCC | 0.74 ± 0.08 a          | 30 ± 6 b                | 0.025 ± 0.003 ab      |
| G + 3% NCC | 0.54 ± 0.06 a          | 25 ± 6 ab               | 0.022 ± 0.002 a       |
| G + 5% NCC | 0.99 ± 0.02 b          | 14 ± 3 a                | 0.074 ± 0.015 c       |
| S + 0% NCC | 4.11 ± 0.88 bc         | 92 ± 7 d                | 0.044 ± 0.006 b       |
| S + 3% NCC | 3.17 ± 0.01 b          | 48 ± 5 c                | 0.067 ± 0.006 c       |
| S + 5% NCC | 4.69 ± 0.30 c          | 56 ± 10 c               | 0.084 ± 0.009 c       |

The mean value of treatment denoted by the same letter indicates no significant difference at the 5% test level according to the Duncan test. 
G = Glycerol; S = Sorbitol; NCC = Nanocrystalline cellulose
increasing the tensile strength. The increase in mechanical characteristics occurred because of the good interaction between NCC and the starch matrix.\textsuperscript{[11]} Thus, it formed strong NCC-starch percolation network formation through hydrogen bonds. In terms of elongation, in general, the sorbitol plasticized film was significantly higher than glycerol plasticized film. This value fulfilled with JIS Standard\textsuperscript{[25]} where values above 50\% have very good elongation. Subsequently, the addition of 5\% NCC concentration increased the tensile strength, but it decreased the percent elongation. The decrease in percent elongation with the increase in NCC concentration was caused by the rigid nature of the NCC nanofiller, which prevents the movement of the polymer matrix.\textsuperscript{[23]} Besides increasing tensile strength, strong interaction through hydrogen bonds between NCC could be also caused by the formation of a rigid network that limited the film matrix motion and reduced the percentage of elongation.\textsuperscript{[12,33]} Research by Abdollahi et al.,\textsuperscript{[33]} Chaichi et al.,\textsuperscript{[11]} Chang et al.\textsuperscript{[36]} stated that the addition of 5\% NCC to the film matrix made an increase in the maximum tensile strength and a decrease in the lowest percentage of elongation. In Table 3, on the whole, the young’s modulus of sorbitol plasticized film with 3\% NCC was significantly higher than glycerol with 3\% NCC. It could be attributed to the higher $T_g$ of sorbitol plasticizer film with high molecular weight. This was complied with a previous study that reported $T_g$ for sorbitol plasticized film was higher than glycerol (as measured by DMA)\textsuperscript{[8]} because the crystal domain acted as a cross-link, limiting amylpectin’s amorphous region’s relaxation, increasing in $T_g$ value and young’s modulus film. This was consistent with Stachowiak N et al.\textsuperscript{[17]} who found that the young’s modulus of sorbitol plasticized film was higher than glycerol plasticized film. This was presumably that glycerol had a shorter carbon chain than sorbitol, changed in polymer positions were easier in the presence of glycerol. As a result, the plasticized matrix had become extremely flexible, plasticizers in the blends penetrated between the polymer chains, reducing intermolecular forces and allowing the macromolecules to slide. The young’s modulus was the opposite of the percentage of elongation, if the young’s modulus decreased, the flexibility of the nanocomposite films increased.\textsuperscript{[37]} Generally, the young’s modulus value increased with increasing NCC concentration, both for glycerol and sorbitol plasticized films. The young modulus of 3\% and 5\% NCC in sorbitol plasticized film and 5\% NCC in glycerol plasticized film was significantly higher than the others. It was due to physical cross-linking caused by the crystallization process so that this amorphous amylpectin chain had limited mobility. As a result, the increase in $T_g$ was a direct result of the amylpectin chain’s decrease flexibility in the presence of crystalline NCC and crystalline amylpectin domains. As the filler content increases, the size of the crystal domain expands, resulting in better bonds and a higher modulus.\textsuperscript{[8,12,38]} In this research, the mechanical properties of sorbitol plasticized film reinforced with 5\% NCC with a tensile strength of 4.69 MPa and elongation of 56\% had the best properties among other treatments and were not much different from several previous studies such as in Kaushik & Kaur.\textsuperscript{[8]} which produced a tensile strength of about 1.5 - 4.75 MPa and an elongation of about 23 - 43\%, while research Noshiro et al. 12 produced a tensile strength of around 2.89 - 4.93 MPa and an elongation of around 57.56 - 83.17\%, in addition, research Miranda et al. 38 produced a tensile strength of about 3.2 - 6.2 MPa and an elongation of about 21.90 - 28.97\%.

\textbf{Scanning Electron Microscope (SEM)}

SEM images of the surface and cross-section of the bionanocomposite films are presented in Figure 2. The surface of the glycerol plasticized film with 0\% NCC (a,g) saw rough and hollow, whereas the surface of the sorbitol plasticized film with 0\% NCC (d,j) saw more fibrous with long tortuous grooves. After the addition of NCC filler, the voids and fibrous paths in the glycerol/sorbitol plasticized film with 3\% and 5\% NCC (b,c, e,f) were reduced because they were filled with NCC so that the surface and cross-section of the film became more homogeneous, compact, dense, and continuous. This was suspected by the presence of NCC which forms a strong network structure through intra and intermolecular hydrogen bonds and reciprocal bonds with the starch matrix and plasticizers. The NCC filler appears to enter the hollow area so that the surface of
the film becomes denser and more homogeneous. According to Kaushik & Kaur [8], the compactness of this film was due to the good adhesion between the filler and the polymer matrix and the interaction of hydrogen bonds between the hydroxyl groups of each component. The results of micrographs of films plasticized glycerol and sorbitol with 5% NCC (c, i,f,l) show that the distribution of NCC was more evenly distributed in the film matrix. Furthermore, the matrix of sorbitol plasticized film with 5% NCC appears to have a strong and dense percolation network due to proper dispersion and compatibility between components. This was presumably because sorbitol could form more stable hydrogen bonds with starch and facilitate stronger interactions between the starch matrix and the NCC surface. Bardet et al. [39] investigated the interaction of NCC and plasticizer (PEG) caused by the interaction between NCC-PEG due to PEG adsorption on the NCC surface.

**ATR-FTIR Spectroscopy**

During processing and drying, hydrogen bonds were formed between the starch-plasticizer-NCC matrix, these new hydrogen bonds were formed between hydroxyl groups in starch, hydroxyl groups in plasticizers (glycerol/sorbitol), and hydroxyl groups in NCC fillers. Strong bonding through hydrogen bonding of these three components results in a strong and rigid network in the film matrix. This interaction provides stability and resistance to films of starch-plasticizer-NCC.

The functional groups and molecular interactions between starch, plasticizer, and NCC in the film matrix can be observed through FTIR spectroscopy (Figure 3). The spectrum of all film treatments showed a widening absorption band in the region of 3281.3 - 3282.9 which was the OH vibration, this indicated the presence of intermolecular and intramolecular hydrogen bonds in the polymer matrix. [40] This band was formed from hydrogen bonds of hydroxyl groups. [41] The addition of sorbitol plasticizer with 5% NCC in the film matrix caused the OH absorption band to be higher than the other treatments. This caused an increase in hydrogen bonding in the film which showed a higher number of hydroxyl groups. Furthermore, the absorption peak was found in the region 2922.2 - 2929.7 which indicated a strong stretching of the C-H bond. The maximum C-H stretching was found in the glycerol plasticized film with 5% NCC. The next absorption peak was found in the region 1576.1-1693.3 which indicated the presence of a C=C bond strain. Also, the absorption peak was found in the region 999.9-1018.9 which corresponded to the strong C-O bond strain. The shift in the absorption band in this infrared spectrum indicated the new interaction between starch, plasticizer, and NCC components that affected in surface properties and characteristics of the film.

**Conclusion**

In the present study, it could be concluded that the differences in molecular weight, the number of hydroxide groups, hydrophilicity from glycerol and sorbitol plasticizer, as well as their compatibility with polymers, could affect the interaction between plasticizer, filler, and polymer to affect the properties of corn starch-based bionanocomposite films. Also, NCC had the accessible hydroxyl groups on the surface, it will interact with the hydroxyl groups of the plasticizers, changing the morphology and imparting new properties. In this research, the addition of glycerol and sorbitol plasticizer reinforced by nanocrystalline cellulose could improve the physical, mechanical, and barrier properties of bionanocomposite films based on corn starch. In this case, plasticizers more markedly affected the elongation properties of the films by reducing internal hydrogen bonds and increasing intermolecular distances in the polymer chains, thereby increasing the elasticity of the films. Meanwhile, NCC more significantly affected the film’s tensile strength by forming a strong NCC-starch percolation network through hydrogen bonds and limiting the motion of the film matrix chain. Also, NCC more markedly affected the WVTR of the film by forming tortuosity structures and long winding paths in the film matrix thereby increasing the water resistance. The sorbitol plasticized film reinforced by 5% NCC was the most effective to improve the properties with the thickness by 0.256 mm; the color values L*, a*, and b* 97.43, −0.04, 1.85 respectively; the water vapor transmission rate 2.259 g/m².h; the water solubility 30.728%; tensile
strength by 4.69 MPa; elongation at break 56%; and young’s modulus 0.08 MPa. This film had a low WVTR value and high tensile strength and elongation, it was suitable for packaging dry products such as instant dry seasoning, instant dry spices, cream soup, etc, that require low permeability and high tensile strength to maintain quality and extend shelf life of the product. Therefore, this provides a great opportunity for the development of bionanocomposite films as biodegradable packaging in the future.

**Disclosure statement**

No potential conflict of interest was reported by the author(s).

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