Mechanical properties of bioplastic form cellulose nanocrystal (CNC) mangosteen peel using glycerol as plasticizer

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Abstract. The environmental problem due to plastic waste had become serious because it could not be recycled neither be degraded naturally by microbe in land. Thus, in the present study, a bioplastic was produced based on cassava starch as the matrix and cellulose nanocrystal (CNC) from Mangosteen peel as reinforcing filler. The CNC was added into the bioplastic with varied concentration at 1 g (BP2), 2.5 g (BP3), 5 g (BP4) and without CNC as BP1. The isolation of CNC followed series of steps (delignification, bleaching, hydrolysis and sonication) before added to the matrix. The effect of CNC addition towards mechanical properties was determined using universal testing machine (UTM) and analyzed using Fourier transform infrared (FTIR) spectroscopy. Results showed that the FTIR analysis confirmed an absorption pattern of cellulose in the starch/CNC bioplastic matrix whereas the effect in tensile strength, tensile modulus and elongation at break were compared to the pure bioplastic without CNC. The highest tensile strength peaked at 1.93 MPa while Young’s modulus at 26.82 GPa was observed for BP1. On the contrary, the addition of CNC fillers to the bioplastics increased the elongation at break and the density while the elongation at break reached the lowest percentage is 13.93% and the lowest density value is 952.5 kg/m3. Based on overall observation, this study proved that the addition of CNC on the other hand the mechanical properties showed the different result.

1. Introduction
The demand on petroleum-based plastic keeps increasing despite of its depleted fossil resource. Plastic faces various environmental problems because it neither be recycled nor degrade naturally by microbe in land, so that plastic waste stacking that causes contamination and degradation on environment [1]. Replacing petroleum-based plastic to bioplastic is a convenient idea as it is eco-friendly to the environment and can be obtained at low cost. In fact, they allow reducing the global dependence on fossil petrol sources for their production and at the same time they provide composting as a simple and sustainable disposal option [2]. In an effort to reduce environmental impacts, biodegradable plastics from renewable resources logically represent the best possibility. Bioplastics seem an attractive eco-friendly alternative plastic since they can be easily degraded by the enzymes [3].

In the production of bioplastic, starch was usually used as it can behave like a thermoplastic in the presence of plasticizer [4]. However, contrarily, the characteristics of starch-based bioplastic are still weak compared to petroleum-based plastics because they have downside of mechanical properties which is starch-based bioplastics are still rigid and low strength. Therefore, to overcome the weakness of
starch-based bioplastics, the plasticisers are generally added to the starch to improve its flexibility, workability and reduces brittleness when it equilibrated at ambient relative humidity. Plasticizer such as glycerol produced strong bond with water molecules thus, provides high solubility of bioplastic film to improve its strength and flexibility [11]. As starch contain of amylose and amylopectin molecules, vinegar (acetate acid) was usually added to help the branched amylopectin molecules to break into straight chained amylose molecules.

Filler also needs to be added to strengthen the bioplastic product. Fillers derived from cellulosic materials was proven can increase the mechanical strength of bioplastic. Besides, this filler can reinforce thermoplastic starch and reduces its hydrophilic character [5]. It can attract considerable interest due to its sustainability, renewability, biocompatibility and it can be considered as a green alternative to fossil-fuel based polymers. In the present study, mangosteen peel was chosen as filler. Mangosteen (Garcinia mangostana) which consists of 17% of outer pericarp, 48% of inner pericarp, 31% of flesh and 4% of cap can be utilized as filler in the bioplastic production. None of study had done on Mangosteen in the production of bioplastic besides of its reported health benefits.

In this present study, nanometer-sized of cellulose which can also be called as cellulose nanocrystals (CNCs) is used as filler in the bioplastic. CNC films are highly hydrophilic and this property can limit their applications in certain areas [6]. The thickness of CNC ultrathin films changed proportional to the changes in relative humidity. At the point of hydration, each individual CNC in the film became enveloped by a 1 nm thick layer of adsorbed water vapour. In addition, the CNC has excellent performance on mechanical properties of bioplastic including of tensile strength and elongation at break. It also provides low density bioplastic and decrease in the water absorption because of its high crystallinity in the fillers [8]. Besides, CNC also have renewable character (as the source comes off of a fruit peel waste), great abundance, high specific resistance and a biodegradability material with a low cost, environmentally friendly and the nanoscale dimensions of the filler keeps the transparency of the material if inherent for the neat matrix [5].

The CNCs are reported to be excellent materials because cellulose possesses fascinating characteristics such as sustainability, biocompatibility, biodegradability, nontoxicity, and easy surface modification. The crystallinity was also increase when CNC added [9]. However, only few studies had examined the effect of incorporation of CNC in the polymer blend. Due to various advantages of CNC can offer, the present study main goal is to introduce CNC from mangosteen peel as reinforcement in polymeric application. Hence, this study addresses the isolation and characterization of CNCs from mangosteen peel and its application as reinforcing filler in starch-based bioplastic. Besides, the effect of different composition of CNC in bioplastic was thoroughly investigated. The resulted study will be presented in terms of its mechanical including of tensile strength and elongation at break, density properties. Other than that, this study also aims to investigate the maximum water uptake of the bioplastic film.

2. Materials and Methods
2.1 Materials
Mangosteen fruits and cassava starch were obtained from the local market in Masai, Johor. In the production of bioplastic films, chemicals including of 99% Glycerol (Qrec) as the plasticiser and Acetic acid (CH₃COOH, Qrec) were used. The CNC was produced using chemicals as follow: Sodium acetate trihydrate (C₂H₃NaO₃, Qrec), 1.0 M Acetic acid, 1.0 M Hydrochloric acid (HCl), 95%-97% Sulphuric acid (H₂SO₄, Qrec), 0.1 mol/L Sodium hydroxide (NaOH, Qrec) and Sodium hypochlorite (NaOCl) which acts as a bleaching agent.

2.2 Preparation of the material
The Mangosteen peels were removed from the flesh by using a knife. The peels were sun dried for about 48 hours at room temperature. Then, the dried Mangosteen peels were grinded and were sieved into 250 μm. The Mangosteen peel powder was stored in a closed container before used. Acetate buffer was produced by adding 7.8 g of C₂H₃NaO₃ in 800 mL of distilled water. Then, 0.5 mL of 1.0 M CH₃COOH
was added before the mixture was stirred constantly. Solution was adjusted to the desired pH using pH meter by addition of 1.0 M HCl.

2.3 Preparation of cellulose fibers by delignification and bleaching
About 50 grams of the Mangosteen peel powder was placed into 1 L beaker and treated with 700 mL of 0.1 M NaOH solution. The mixture was heated with a constant stirring for 2 hours at a temperature range of 60-65°C. Then, the mixture was filtered and washed several times to separate the insoluble pulp and the excess NaOH. The insoluble pulps were then bleached with 500 mL of NaOCl buffered to a pH 5. The bleached fibre was washed for thrice with the distilled water until it becomes neutral. Then, the cellulose fibres were air dried for 2 days and weighed.

2.4 Isolation of CNC by acid hydrolysis
About 10 grams of the bleached Mangosteen fibre were hydrolysed in 100 mL of 95% H₂SO₄ at 50°C for 45 min with constant stirring. Then, the hydrolysed cellulose was diluted with cold distilled water to stop any further reaction. It was then centrifuged in centrifugal Kubota 5500 three times at 10,000 rpm and 10°C for 10 min. Next, sonication was then carried out to disperse nanocrystals for every 100 mL using Elmasonic P for 6 min, 37 kHz and 80% of power. The resulting suspension CNC was dried in a freeze drier at 3°C and kept for further use.

About 10 g of cassava starch was dissolved in 60 mL distilled water. Then, 5 mL of vinegar was added to 7 mL of glycerol before CNC was mixed together at different concentration. The solution was stirred for a few minutes with a low to high temperature (105°C to 200°C). The mixture was continuously stirred until it become viscous then spread into mould. Different bioplastic films were prepared according to Table 1. The bioplastic samples were then dried at room temperature.

Table 1. The composition of materials for different bioplastic film.

| Material       | Composition (wt%) |
|----------------|-------------------|
|                | BP1   | BP2   | BP3   | BP4   |
| Cassava starch | 45    | 43    | 41    | 37    |
| Glycerol       | 32    | 31    | 29    | 26    |
| White vinegar  | 23    | 22    | 20    | 18    |
| CNC            | 0     | 4     | 10    | 19    |

2.5 Fourier transform infrared spectroscopy (FTIR)
The characterization of isolated CNCs was analysed using (Bruker Vertex 70) FTIR analyser to study the molecular structure of the BP film at different CNC concentration and without CNC. Solid sample weighting between 1-2 mg were placed on the test are. The FTIR spectrum results were recorded from 4000 to 400 cm⁻¹ with 40 scans and 4 cm⁻¹ resolution.

2.6 Mechanical characteristics of starch-CNC bioplastic film
2.6.1 Tensile strength and elongation at break
The bioplastic film was cut into 7 cm × 1 cm to measure the tensile strength and elongation at break according to ASTM D882-91 standard for bioplastic. The Universal Testing Machine (UTM) was used with slight modification with the gauge 3 cm, and conducted with the speed of 12.5 mm/min. The values of tensile strength were obtained from the observed data. Meanwhile, elongation at break is an indication of bioplastics flexibility and is expressed in percentage.

2.6.2 Young’s Modulus
Young’s Modulus (E) or the modulus of elasticity was determined using the same method with Tensile strength. Samples with dimension of 7 cm in length, 1 cm in width, and 0.9 mm in thickness were cut manually. Films were then stretched by GoTech UTM at a speed of 12.5 mm/min. Then, the modulus
can be calculated from tensile stress and tensile strain derived from load/extension graphs that was obtained from UTM.

3 Results and Discussion

3.1 FTIR Characterization

The infrared obtained from the CNC and BP films are depicted in and the band assignments based on literature are given in the corresponding Figure 1. The FTIR was used as analytical method to study the molecular structure and to compare it between pure CNC and at different concentration of CNC in BP. Based on the results obtained, all spectra of BP films show the presence of four major peaks of OH, CH, CO and OH (deflection of water). The similar peak was observed for pure CNC spectrum with previous study of Augustin et al. [5]. There is some change in broad of the wavelength of the groups when CNC was added to BP due to the mass of the molecules reduced since the frequency of vibration is inversely proportional to mass of vibrating molecules [5]. The peaks discovered between 3100 to 3700 cm⁻¹ represent to the hydrogen bonded hydroxyl group(O-H) due to the complex vibrational stretching that occurs in the carbohydrate structure. It is also expected that there is some interaction of hydrogen bonding of OH groups. The broadening of OH groups which observed by Fig 1(c) to (e) might be due to the interaction of CNC with the glycerol and starch. This similar band had been proved from the previous study of Sultan & Johari [6]. The band was shifted to high wave number in the presence of 2.5g CNC which leads to decreasing in intermolecular hydrogen bonding but the wave number started to decrease when 5 g of CNC was added. This shows that CNC does not affect the molecule at high quantity. The spectrum of OH which present in the bioplastic also be reported by Mendes et al. [10].

The –CH stretching was obtained at 2326 cm⁻¹ which represent the starch structure which existed in all BP samples. The bands at approximately at 2850 to 3000 cm⁻¹ indicates the C-H bond stretching of CH₂ groups. It is expected that the band of 1740 cm⁻¹ should present which representing cellulose and hemicelluloses. In contrary, this band was not reported, and it is as expected since the cellulose had turn into nanocystal.

The peak band at 1616 cm⁻¹ which representing lignin was found in pure CNC was disappeared after chemical treatment due to partial removal of hemicelluloses. The absorption band at 1580 to 1700 cm⁻¹ is representing the adsorption of water that also attributed to hydroxyl bending in water molecules. This peak becomes weakened after the chemical treatment. It might also result of decreasing in peak intensity influence by partial removal of hemicelluloses. Besides, according to Zuraida et al., another peak between 999 cm⁻¹ and 1020 cm⁻¹ are attributed to C-O bond stretching of C-O-C group [29]. The peaks were shifted from 1002.94, 1018.37, 1022.26 and 1002.94 cm⁻¹ respectively. This can be concluded that a more stable of hydrogen bond can be formed by glycerol during BP production. FTIR spectra of polymer blends enabled the study of interaction between components where lower wave number indicates stronger interaction between components. Miscible polymers can cause different interaction of hydrogen bonding that bring changes in band shifting and broadening as expected from result.
3.2 Mechanical characteristics of starch-CNC bioplastic film

3.2.1 Tensile strength and elongation at break

Based on Figure 2, the tensile strength of pure bioplastic film BP1 was found to be 1.93 MPa while the tensile strength of three other bioplastic films was found to be slightly lower than BP1. The graph shows the decreasing in the tensile strength with an increase of CNC fillers. This condition occurred may be due to the presence of agglomeration of CNC particles into the starch matrix that caused deflection in bioplastic film, BP3. In spite of this, Talja et al., 2008 proposed that the trend of tensile strength increases gradually with addition of CNC fillers because the presence of crystallization fillers can improve mechanical properties of bioplastic film. However, BP4 has higher tensile strength than BP3 which follows most of articles view about the effect on the bioplastic film with an addition of crystalline fillers, the tensile strength will increase [7]. This showed that the improvement of bioplastic mechanical properties can be attributed to good interfacial adhesion that can form strong hydrogen bond network between starch matrix and CNC fillers.

Meanwhile, Fig. 3 shows the effect of elongation at break of bioplastic film based on different mass of CNC content. The elongation at break of BP1 reached 13.93% which slightly lower than BP2 at 20.13%. This is because CNC that contain in the bioplastic film acts as filler in the film and increase the effect of elongation at break. However, BP3 reached 21.06% which is higher than BP4 that only reached 16.93%. This result shows inconsistent as there is high and low trend on the effect of elongation at break. It was possibly due to agglomeration of the fillers that contains in bioplastic film that can cause the inconsistency of the result. The agglomeration of the Nano-fillers occurred on the surface of bioplastic film might be due to the poor dispersion of the cellulose whiskers in the organic solvent of bioplastic which may be increased by surface modification of CNC. Based on the Figure 3, the best result of elongation at break are between BP2 and BP3. This is because with the addition of CNC in the bioplastic film may resulted in a higher strength and lowered the elongation at break. This may due to hydrogen bond between hydroxyl and carboxyl group (COOH) of cellulose and hydroxyl (O-H) group from starch [11].
The good result of CNC was due to proper interaction between starch, citric acid and cellulose at appropriate concentration. Hence, based on this view, the other possible cause that affect the trend of elongation at break that seem irregular can be the inappropriate procedure on the preparation of cellulose that caused the improper interaction between starch, citric acid and cellulose in the bioplastic film. Generally, the mechanical properties of bioplastic starch-based can be improved with the addition of cellulose fillers because starch alone cannot form film with the satisfactory mechanical properties unless with the addition of fillers and plasticisers such as glycerol [12]. When the tensile strength increased, the elongation at break will be decreased. The main contribution of the good strength results is contributed by the hydrogen bonding between the fillers and starch matrix [7]. Moreover, the concentration of the fillers also can influences the results.

3.2.2 Young Modulus
Young’s modulus was determined to evaluate improvements in the mechanical stiffness as CNC was added to the bioplastic as shown in Figure 4. BP1 has the highest value of tensile modulus despite its absence of CNC content in the film [15]. This means that the increasing amount of CNC in the bioplastic films resulted in decreasing its modulus. Crystalline materials are known to have high stiffness and have been proved that a significant increase in tensile modulus can be achieved in the addition of crystalline materials [13]. Depending on the size of the particles, the shape and its aspect ratio (length or diameter) a solid material added to a plastic may or may not act as a reinforced. Not all fillers, which in this project are cellulose nano-cystals which were extracted from Mangosteen peels, can increase the mechanical properties of plastics. This explains why the graph that was obtained shows a fluctuating result. It is also apparent that the size ratio has a pronounced effect on the moduli. With the nano-size filler particles (and a lower size ratio), the increase of the storage modulus relative to the polymer for a given filler content is greater when compared to the increase obtained for μm-size filler particles [14]. Another factor that can cause the decreasing values of Young’s modulus is the amount and the type of plasticiser added into the bioplastic [16]. Although it was maintained for all 4 films, it could also lead to the problem of having less elongation modulus than of BP1 which contains no CNC. The usage of glycerol as the plasticiser might be not suitable with the properties of CNC which can result in decreasing tensile modulus. Crystallinity of starch film has been shown to increase with decreasing plasticizer content [15].
4. Conclusion

As a conclusion, the bioplastic films reinforced with CNC from mongosteen in BP has shown a good performance than the BP without CNC. The FTIR shows functional groups of four major peaks (O-H, C-H, C-O and O-H(deflection of water)) that been discovered where the interaction between components was determined but these interactions were not too significant to cause higher peak shifts. This study elaborates the mechanical properties of the bioplastic films which include the high tensile strength, high tensile modulus, low elongation at break and low density. Results show the decreasing trend which the higher the amount of CNC, the lower its mechanical properties. The mechanical characteristic of the pure starch bioplastic has the highest tensile strength and lowest elongation at break as compared to others. The density of bioplastics decreased as CNC content increased, but this study shows a fluctuating result. This is because it depends on the preparation of the bioplastic because it can affect the interaction of the fillers and the bioplastic matrix. The loss of soluble matter shows an increasing result as the amount of CNC addition increased. In the water uptake capacity, the range of the bioplastic water absorption is between 40 – 50%.

References

[1] Vince J and Stoett P 2018 From problem to crisis to interdisciplinary solutions: Plastic marine debris *Mar. Policy.* **96**, p. 200-203.

[2] Marina Arrieta L López J A L López D Kenny J and Peponi 2016 Biodegradable electrospun bionanocomposite fibers based on plasticized PLA–PHB blends reinforced with cellulose nanocrystals *Sci. Rep.* **93**, 1 p. 290–301.

[3] Rohan G U and D’souza L 2018 Bioplastics A Step towards Sustainability *Int. J. Curr. Trends Sci. Technol.* **8**, 5 p. 20211–20218.

[4] Thaisa M A MoroJosé L R Ascheri Juan A R Carlos O Carvalho W P and Meléndez-Arévalo A 2017 Bioplastics of Native Starches Reinforced with Passion Fruit Peel *Food Bioprocess Technol.* **10**, 10 p. 1798–1808.

[5] Melissa S M A Augustin B and Ahmmad B 2014 Bioplastic based on starch and cellulose nanocrystals from rice straw *J. Reinf. Plast. Compos.* **33**, 24 p. 2205–2213.

[6] Nagy S Csiszár E Kun D and Koczka B 2018 Cellulose nanocrystal/amino-aldehyde biocomposite films *Carbohydr. Polym.* **194**, p. 51–60.

[7] Maulida M Siagian and Tarigan P 2016 Production of Starch Based Bioplastic from Cassava Peel Reinforced with Microcrystalline Cellulose Avicel PH101 Using Sorbitol as Plasticizer *J.
Wu J Nagarajan H Shu S Zhang J Zhou T Duan L and Zhang Y 2018 Green and facile surface modification of cellulose nanocrystal as the route to produce poly(lactic acid) nanocomposites with improved properties Carbohydr. Polym. 197, p. 204–214.

Sonal L M M Karkhanisa S Starkb M N Sabob R C 2018 Water vapor and oxygen barrier properties of extrusion-blown poly(lactic acid)/cellulose nanocrystals nanocomposite films Compos. Part A Appl. Sci. Manuf. 114, p. 204–211.

Mendes J F 2016 Biodegradable polymer blends based on corn starch and thermoplastic chitosan processed by extrusion 137, p. 452–458.

Maulida M S and Tarigan P 2016 Production of Starch Based Bioplastic from Cassava Peel Reinforced with Microcrystalline Cellulose Avicel PH101 Using Sorbitol as Plasticizer J. of Phy.Conf. Series. IOP Proc. 12.

Zhong Y 2017 Comparison of gelatinization method, starch concentration, and plasticizer on physical properties of high-amylose starch films J. Food Process Eng. 41, p. 12645.

Zárate-ramírez L S Romero A Bengoechea C Partal P and Guerrero A 2014 Thermo-mechanical and hydrophilic properties of polysaccharide / gluten-based bioplastics Carbohydr. Polym. 112, p. 24–31.

Makepeace D K Locatelli P Lindsay C Adams J M and Keddie J L 2018 Colloidal polymer composites: Are nano-fillers always better for improving mechanical properties J. Colloid Interface Sci. 523, p. 45–55.

Nagy S Csiszár E D Kun D and Koczka B 2018 Cellulose nanocrystal/amino-aldehyde biocomposite films Carbohydr. Polym. 194, p. 51–60.

Muhammad A Rashidi A R Roslan A and Idris S A 2017 Development of bio based plastic materials for packaging from soybeans waste AIP Conf. Proc. 1885, p. 1-9.