Cassava starch/carboxymethylcellulose biocomposite film for food paper packaging incorporated with turmeric oil

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Abstract. Issues related to the performance and processing remain a challenge when managing materials from renewable and natural resources. This study aims to show the potential of biopolymer film composite from cassava starch and carboxymethylcellulose to replace the synthetic coating and the area of studies are its barrier, mechanical and chemical properties. Fourier Transform Infrared analysis identified that only film containing CMC could act as antimicrobial agent carrier. The biopolymer film coated on the kraft paper with the presence of 30% v/v glycerol and 10% w/w CMC had the highest tensile strength, at 15 MPa. The film-coated paper also exhibited a hydrophobic surface with reduction of the contact angle from 104.95° to 96.33° for 120 seconds. Meanwhile, addition of turmeric oil into developed BF 3 showed insignificant changes in tensile strength but reduced the contact angle to less than 90°. Thus, the formulated coating materials can be used as an alternative green technology for paper coating used in food industry and can be classified as a form of active packaging.

1. Introduction
Most of the researches have been conducted with the goal of infusing food additives into the food packaging to maintain the quality of food and elongate the usability period of these foods by inhibiting the microbial growth [1, 2]. This system of packaging is recognized as active packaging, where it inhibits the microbial development in non-sterilized food and pasteurize food, while avoiding food contamination during the post-processing [3]. Recent studies discovered that additives extracted from plants with medicinal properties possess an inhibitory effect on various types of microorganism [4]. The examples include Curcuma longa L., Labisia pumila, Morinda citrifolia L. etc. This antimicrobial property can be attributed to the large number of secondary metabolites found in spices and herbs which have the ability to impede the growth of the infectious organisms [5, 6].

Cassava starch has a very good potential in term of domestic demand. A study on cassava starch by Parra [7] discovered that films based on cassava starch have good flexibility and low water permeability. This conforms with the study done by Maran et al. [8] where the authors indicated that cassava starch has great potential as the starch material for the production of biopolymer film and coating because it exhibits film-forming properties with great biodegradability. However, film with a high concentration of starch may recrystallize and become brittle during long-term storage, hence reducing its value [9]. This is in agreement with study by Kester [10], where starch-based films possess poor mechanical strength after a period of time due to the retrogradation process of the molecular chain. The drawback of starch as a biopolymer base can be overcome by adding a stabilizer or by mixing it with other biopolymer bases as mentioned by Kester [10].

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Fortunately, this problem can be solved by adding plasticisers to improve the biopolymers workability and realise the full potential of starch [11–13]. The council of International Union of Pure and Applied Chemistry (IUPAC) has defined plasticiser as a material or substance that improves workability and flexibility of material such as plastic or elastomer. Hydrophilic compounds with low molecular weight such as glycerol and sorbitol are commonly used as biodegradable plasticisers in starch films. From the literature review, glycerol is the most incorporated component in hydrocolloid films including films based on cassava starch [11–14]. Through their experiments, Ahmad et al. [15] shown that tensile strength of thermoplastic sago starch increases with increasing amount of glycerol. Vieira et al. [9] have also stated that the crystallisation of potato starch containing glycerol can significantly affect the mechanical properties of the plastic sheet. This can be attributed to the formation of the entangled starch matrix and starch chain-to-chain associations as plasticiser content is increased.

Ghanbarzadeh et al. [16] stated that single based biopolymer films from a single source of biopolymer may possess good properties in some aspects but poor in others. This issue will be a great obstacle in a full-scale industrial application. Hence, researchers suggested the biopolymer to be mixed with other biopolymers in order to enhance the performance of bio-based coatings [17]. The films produced by the blending of biopolymers from polysaccharide with protein, polysaccharide with lipid, or even polysaccharide with polysaccharide sources are known as biocomposite films. A study by Alves et al. [18] on corn starch film had proven that the films by themselves are unsuitable for packaging purposes as they possess poor mechanical properties and are highly sensitive to water [18]. Meanwhile, a study by Guo et al. [19] on composite films by blending corn starch with carboxymethylcellulose (CMC) shown that the film mechanical properties have improved twice compared to the corn starch film itself [20]. CMC is suitable for film blending with other biopolymers due to its non-toxic, non-allergenic and high viscosity properties as well as its ability to act as a filler to improve barrier and mechanical properties [16, 21].

Cassava starch as film based has been tested in multiple studies on essential oil of cinnamon, lemongrass, ginger and Curcuma xanthorrhiza Roxburgh as antimicrobial agents [11-14]. A study by Dani et al. [25] on cassava starch biopolymer film incorporated with lemongrass oil stated that Trichoderma and Penicillium will not appear until the third day of incubation and the films are capable of reducing the microbial count on meat during storage. However, adding more lemongrass oil will lead to reduced tensile strength and roughness of the biopolymer film. In addition, Rojas et al. [25] also highlighted that the presence of essential oil from plants can significantly modify the tensile properties but would not affect the permeability of oxygen and water vapour of the films. Therefore, in this study, the performance of the composite biopolymer film incorporated with turmeric oil was characterised on its tensile strength, surface wettability and stability in releasing turmeric oil by using Fourier Transform Infrared (FTIR) analysis.

2. Materials and methodology

2.1. Materials

Commercial cassava starch (Cap Kapal ABC.Co, Thailand) was applied as primary biopolymer, glycerol (Merck, Germany) as plasticizer, carboxymethylcellulose (CMC) as composite biopolymer which was kindly provided by Waris NOVE Sdn. Bhd., Pahang, Malaysia and turmeric oil as antimicrobial agent sources. Unbleached kraft paper (Muda Packaging, Malaysia) was used as the paper food packaging material.

2.2. Biopolymer film preparations

Film-forming solutions was prepared by cassava starch gelatinization (5%) at a temperature of 75°C ± 5°C for 20 mins under continuous stirring at 500 rpm before being plasticized with glycerol (30% w/w of starch). Meanwhile, 10% w/w CMC was dissolved in 100 mL distilled water at room temperature. Then, both of the solutions were mixed and slowly stirred at 250 rpm for 20 minutes at 40°C to ensure the mixture was completely mixed. Turmeric oil (0.15% v/v) was added and stirred for another 20
minutes. The film-forming solutions were then casted at volumes of 30 mL on kraft paper (30 cm length × 15 cm width) using an automatic film casting machine at a speed of 1 cm/s for blade distance of 1.25 mm, respectively. After that, the wet-coated paper was dried at 50°C for two and half hours and conditioned in a desiccator at 25 ± 5°C for 24 hours prior to sample analysis.

2.3. Fourier transform infrared analysis

The disruption on the functional group of starch-based film affected by the different content of CMC on the starch based film were analyzed by using the Fourier Transform Infrared (FTIR) spectroscopy (Perkin Elmer, USA) at wave number ranging from 400 to 4000 cm⁻¹. The sample preparation of the biopolymer films was done by poured 30 mL of film-forming solutions in disposable Petri dish (90 mm × 15 mm). Next, the solutions were dried at 50°C until the weight of the samples was constant. The sample port was cleaned by using acetone to remove any variation caused by contamination on the scanning. The spectrum yields from the sample scanning were collected and studied.

2.4. Tensile strength measurements

Tensile strength measurement studied if the strength of the film-coated paper was sufficient to apply as a food packaging. The mechanical test was conducted using the Tinius Olsen Universal Testing Machine, Model H50KT (USA). Samples were cut into the dimensions of 75 × 25 × 2.5 mm (length × width × thickness) before placing them onto the sample holder. The bottom and upper gaps were tightened. The crosshead speed was set at 50 mm/min with a gauge length of 50 mm. The test was repeated three times. The data were tabulated and plotted using Microsoft Excel. The sequence of procedure is according to ASTM D3500.

2.5. Wettability surface measurements

Wettability analysis was done to identify the hydrophobicity surface of the CS/CMC films by measuring the contact angle of water in contact with the film-coated paper using Video Contact Angle Goniometer (AST Products, INC.). Wettability of film was measured using the contact angle method as suggested by Liu et al. [26]. The samples were cut in rectangular strips with a dimension of 1 cm × 1 cm (width × length). The rectangular strip samples were then directly placed on the horizontal moveable stage and 10 μL of water was dropped onto the film surface using a 500 μL precision micro syringe. For each sample, three measurements were taken and the average values were calculated.

3. Results and discussions

3.1. FTIR analysis of biopolymer films

From the spectre of cassava starch in figure 1, it can be seen that C-OH and C-O-C groups of cassava starch wavenumbers were seen at wavelength 3290 cm⁻¹ and 927 cm⁻¹, respectively. It was expected that the crosslinking reaction of the polymeric chain would occur at these two regions as suggested by Ahmad et al. [15] in a study of sago starch as a biodegradable polymer. The authors suggested that interaction of hydrogen bond formation of the starch with glycerol occurred in the C-OH group and the C-O-C group where the wavenumbers for the C-OH group and the C-O-C group were reduced; indicating that the OH group of starch took part in hydrogen bond formation. The existence of a hydroxyl group at wavenumber of 3281 cm⁻¹ also can be seen in the spectre of CMC, which is expected to contribute in formation of various kinds of intermolecular and intramolecular hydrogen bonds with the hydroxyl group in cassava starch, glycerol and turmeric oil. The formation of hydrogen bond could be attributed to the strength of the film as suggested by Fan et al. [27].

Intermolecular interaction of biopolymer chain with turmeric oil was analysed by using FTIR analysis and shown in figure 1. Referring to figure 1 (a) and (b), there were no presence of phenol group indicated that the intermolecular interaction of turmeric oil with cassava starch film and cassava starch with glycerol film occurred at O-H stretch region which then forming the C-O-C stretch. In contradiction, it can be seen in figure 1 (c) that the intermolecular interaction occurred at regions of C=O stretch and intermolecular bonding of C=O-H as peaks at 1737 cm⁻¹ and 1231 cm⁻¹ were disappeared with addition of turmeric oil into film-forming formulation. At the same time, a new peak
was formed at region of phenol group. This finding indicated that presence of CMC preserve the functional group of phenol which also the major groups of antimicrobial compounds from turmeric oils.

Besides that, the structural property which was displayed as FTIR spectre of cassava starch film and cassava starch with glycerol film significantly deviated with increasing of storage time. This may attributed by formation of hydrogen bond between the polymeric chain with moisture as both glycerol and starch was hydrophilic compounds with high intensity of hydroxyl group. Meanwhile, the structural properties of film containing CMC approximately same as can been observed from the FTIR spectres with increasing of storage time. This was attributed by the formation of intermolecular and intramolecular hydrogen bonds of CMC with the polymer chains was stronger than the hydrogen bond formed with the moisture content. Thus, it can be stated that only cassava starch film with presence of glycerol and CMC could act as antimicrobial agent carrier as it can behold the turmeric oil and allowed it to release at right stipulated period of time such as when there was presence of microbes. This finding is in agreement with study done by Fajardo et al. [28] where they stated that controlled released of additives from polymer matrix was based on the structural characteristic of the film. The functional group of the respective regions was justified accordingly to Coates [29], Gokel [30], Kizil et al. [31] and Fan et al. [27].

Figure 1. FTIR spectre of turmeric oil with different formulation of film during three days of storage (a) Cassava starch, (b) Cassava starch with glycerol and (c) Cassava starch with glycerol and carboxymethylcellulose film.

3.2. Tensile strength measurements
Referring to figure 2, non-plasticized cassava starch film-coated paper (BF 1) had the lowest value of tensile stress, which was 12 MPa, compared with plasticized film-coated paper (BF 2), whose tensile stress value was 12.9 MPa. A similar behaviour regarding the effect of glycerol on film strength was found in a study by Bonilla et al. [32]. The authors stated that generally, as the plasticizer concentration increased, the tensile strength was also increased. It can also be seen in figure 2 that
addition of CMC significantly enhanced the tensile strength. Presence of CMC in starch complex chain contributed in stable dense of biopolymer film as filler. This finding was also supported by Hong [20] in a study on composite films by blending corn starch with CMC. He identified that the film mechanical properties had been improved twice compared with the corn starch film itself. As depicted in figure 2, there is a significant discrepancy between the tensile strength of biopolymer film coatings on the kraft paper without the presence of turmeric oil and those with turmeric oil present. This is because turmeric oil reduced intermolecular interaction of polymeric chain. Similar findings have been found by Maria et al. [25], wherein authors found that the incorporation of essential oil into biopolymer films caused a noteworthy reduction in the tensile strength of biopolymer films.

3.3. Wettability measurements

Figure 3 show that BF 1 had the lowest contact angle distributions throughout 120 seconds, which is lower than 90°. This finding indicates that cassava starch-based film exhibit hydrophilic properties which are not desirable in this study as it increased the affinity of moisture on the film surface. Presence of glycerol reduced the hydrophilicity of the cassava starch-based film with the increase in contact angle throughout 120 seconds of observation. This indicates that the surface affinity of the biopolymer films for water decreased when glycerol was added, which then reduced the water uptake. In light of the results obtained, this is believed to have occurred because the biopolymer film surface of BF 2 remained dense as glycerol filled the intermolecular chains of the biopolymer. A similar behaviour was found in a study by Basiak et al. [33]. The authors stated that the higher the contact angle, the lesser the affinity of water for the film surface as the contact angle represents surface equilibrium among water, air and a biopolymer film surface.

The behaviour of water droplets on the surface of BF 3 with the presence of CMC clearly changed from BF 2 (0% CMC). In addition, only BF 3 exhibited hydrophobic properties, as the contact angle remained higher than 90° over 120 seconds, whereas BF 1 exhibited hydrophilic properties as the contact angle remained lower than 90°. As for BF 2 and BF 4, hydrophobic properties were apparent only when the water was initially dropped, and it started to spread or adsorb into the film with time, exhibiting hydrophilic properties at the end of 120 seconds. Based on the contact angle against water on different sources, the materials were classified as hydrophilic for contact angle values lower than 90° or hydrophobic for contact angle values higher than 90° as reported by a number of researchers [24-26]. This is in agreement with a similar finding reported by Hong et al. [20]. With a lower content of CMC, CMC acted as filler, which allowed it to disperse well in a starch matrix and thus improved the water barrier of the film. Decreased in the contact angle of a water droplet on biopolymer film was observed in figure 3 with increased in volume of turmeric oil. This is mainly due to an increase in hydrophilicity of the biopolymer film. This decrease could be due to reduction in molecular interaction of the biopolymer film with the presence of turmeric oil. This is in agreement with the results reported by Souza et al. [36], in which the authors identified that incorporation of cinnamon essential oil.
decreased the water barrier properties of biodegradable film. This was because introduction of essential oil reduced the molecular interaction between polymeric chains and thus allowed water uptake on the film.

![Figure 3](image-url)  
**Figure 3.** Effects of glycerol, carboxymethylcellulose and turmeric oil on wettability of cassava starch film-coated on the kraft paper

4. Conclusions
The performance of the composite biopolymer film was evaluated on its tensile strength, wettability and the ability of the biopolymer film to act as additive carrier. Tensile strength and wettability measurements indicated that the biopolymer film containing 30% (v/v starch) glycerol and 10% (w/w) CMC labelled as BF 3 had the highest tensile strength (15 MPa) and exhibit hydrophobic properties with contact angle higher than 90° throughout 120 seconds. Meanwhile, addition of turmeric oil into developed BF 3 showed insignificant changes in tensile strength but reduced the contact angle to less than 90°. FTIR analysis on incorporation of turmeric oil in each of starch film, starch with glycerol film, and starch with glycerol and CMC identify that presence of CMC stabilize the intermolecular interaction of the turmeric oil with the complex polymeric chain. Therefore, the results suggested that applying the biopolymer film containing turmeric oil as kraft paper coating may improve its functionality in prolongs the shelf life of foods. Thus, it can be stated that the develop biopolymer film could replace the currently used petroleum based derivative plastic in the food industry.

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