Hydrogel film synthesis for biowrapping via a single-cycle freeze-thaw process untilizing carboxymethyl cellulose/microcrystalline cellulose and citric acid as crosslinker

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Abstract. Crosslinking will be critical in producing the desired hydrogel with good absorption and high mechanical strength properties. Despite chemical crosslinking, the physical technique of freeze-thaw has reduced chemical use. This research determined the appropriate formulation of CMC/MCC and citric acid concentration using the freeze-thaw method of one cycle and drying to produce hydrogel with high water absorption and mechanical strength. The research findings showed that the hydrogel film created for biowrapping must have high absorption capacity and mechanical strength. This was achieved using a CMC/MCC ratio of 90:10 and a 5% citric acid crosslinker concentration. The hydrogel film showed a swelling capacity of 322.72%±9.32 at pH 7, a gel fraction of 9.87%±0.26, and a dry gel rehydration ability of 466.96%±30.41. The tensile strength for the CMC/MCC 90:10 ratio was 0.303±0.001 MPa, and the strain at F max was 48.74%±2.42. The water vapor permeability level was also measured at 3.688×10^{-5} g/m.Pa.24h. Increasing the MCC to CMC ratio to 50:50 led to a decrease in the water vapor permeability of the hydrogel film.

1 Introduction

Cellulose hydrogels can be created from cellulose solutions with the help of physical cross-linking. This is possible because cellulose contains hydroxyl groups, which can form hydrogen bonding networks. Carboxymethyl cellulose (CMC) is commonly used to make hydrogels. Multiple hydroxyl groups in the cellulose molecule allow the formation of crystals held together by hydrogen bonds. There are both intra- and intermolecular hydrogen bonds and van der Waals forces between the non-polar groups in cellulose. [1]

Using cellulose from oil palm empty fruit bunches (OPEFB) to produce hydrogel products remains an area with insufficient information. Cellulose derivatives, including carboxymethyl cellulose and hydroxypropyl cellulose, can be converted into hydrogels

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through chemical and physical crosslinking. Previous research has indicated that using chemical crosslinking could result in stronger and more resilient bonding. However, further investigation into alternatives, such as using organic acids as crosslinkers, is essential to explore cost-effective and safe crosslinking approaches [2].

Crosslinking is crucial for creating a stable cellulose hydrogel structure by forming a network of three-dimensional covalent linkages during gelation. Crosslinking is essential to achieve the desired hydrogel with muscular mechanical strength and sufficient absorption capabilities. Different techniques, such as chemical, radiation, or physical crosslinking, can be used to create hydrogels [3]. Hydrogels with high liquid absorption capacity are synthesized by cross-linking during manufacturing. While unreactive chemicals are removed during cross-linking, most chemicals used as linking agents are hazardous. Crosslinkers such as carboxylic acid and carboxylic anhydride create -COOR bonds, while esterified components like organochlorine, epoxide, and vinyl compounds form R-O-R bond [4]. R-O-R bonds are formed using diglycidyl ether of poly(ethylene glycol) [5] and epichlorohydrin (ECH) [6].

Physical methods such as freeze-thaw and photocrosslinking with UV and gamma radiation are considered alternatives to chemical crosslinking. It is essential to seek crosslinking agents that are safe, affordable, and effective [7]. Physical crosslinks are reversible, meaning the hydrogel will readily dissolve again when the pH, temperature, or ionic strength changes. In contrast, chemical crosslinks are permanent. To produce a robust hydrogel and determine the optimal crosslinking process conditions, studying the combination of chemical and physical crosslinking is essential.

The use of toxic chemicals in the synthesis of hydrogels must be strictly avoided. Therefore, it is essential to explore the synthesis of hydrogels using non-toxic crosslink agents. Citric acid is considered a safe and suitable crosslinking agent for biomaterials in biomedical applications [8]. Additionally, previous research has investigated the synthesis of hydrogels using carboxylic derivatives of succinic acid [2]. When hydrogels are used for biowrapping, they directly interact with food products. Thus, searching for safe chemical crosslinkers is crucial, and several carboxylic acid compounds are available within the green chemistry categories.

This study will utilize citric acid as a crosslinking agent to bond carboxymethyl cellulose and microcrystalline cellulose (MCC). Citric acid is chosen for its carboxylate functional group, which can effectively link with cellulose chains. It is also a cost-effective and environmentally friendly crosslinking agent, addressing the challenges associated with hydrogel production. Furthermore, citric acid is abundantly available in nature and can be produced commercially.

The successful formation of the hydrogel as biowrapping must be able to absorb transpirants and release moisture simultaneously when used to package fresh fruits and vegetables, thereby keeping the food fresh for a longer time. Therefore, the criteria of water absorption ability, tensile strength, and permeability to water vapor must be balanced so that the function of hydrogel film as biowrapping to slow down the respiration of fresh fruit by keeping the fruit moist will be obtained. The downside of PVP-CMC hydrogels for packaging materials is their high permeability to oxygen and water vapor [9]. These properties can be enhanced by incorporating other biofiller components into the polymer structure. This study investigates the optimal proportion of MCC biofiller in CMC-based hydrogels from OPEFB.

2 Materials and Methods

2.1 Materials

OPEFB were supplied from PT Batu Gunung Mulia Putra Agro (BGMPA) South Kalimantan, NaOH (Merck), $NaClO_2$ (Clover Chemicals Ltd), glacial acetic acid (Merck), HCl (Merck), isopropanol (Merck), monocloroacetic acid (MCA) (Merck), ethanol (Merck), methanol (Merck), CMC commercial (Sigma Aldrich) and distilled water. The equipment includes a beaker glass, measuring cup, centrifuge, hotplate stirrer, spatula, filter paper, filter cloth, tube, desiccator, grinder (Getra IC-06B, China), oven (Memmert, Germany), and universal tensile machine.

2.2 Preparation of OPEB.

The OPEFB fibers were manually separated after being washed with hot water. They underwent five additional washes in clean water. To eliminate any remaining oil and dust, the fibers were soaked in a 2% soap solution for five hours, using a fiber-to-soap solution ratio of 1:4 (w/v). The fibers were rinsed twice with clean water to remove soap residue and other impurities. After the washing process, the fibers were drained and dried at 60°C for 48 hours. Once thoroughly cleaned and dried, the OPEFB was milled into 5 cm pieces and sieved to achieve a mesh size of 30.

2.3 Bleaching and delignification process

OPEFB fibers underwent a two-step bleaching process using a 3.22% $NaClO_2$ solution in a 1:25 (w/v) ratio. The temperature of the solution was elevated to approximately 75°C (± 5°). Subsequently, acetic acid was added to adjust the pH to a range of 4 to 4.5, and the mixture was continuously heated at 75°C (± 5°) for one hour. Once the bleaching process was complete, the fibers were dried and weighed. To achieve delignification, the bleached fibers were treated with a 10% NaOH solution at a 1:20 (w/v) ratio at room temperature (30°C). The resulting delignified cellulose was thoroughly washed with distilled water and refluxed for 30 minutes to ensure cleanliness, after which it was dried at 60°C (± 5°) for 24 hours. [10]

2.4 Production of CMC

The slurry formation was used to produce CMC [11]. 5 g of pulp was macerated with NaOH (30%) solution (ratio of cellulose: NaOH 30% =1: 3.36), which was added dropwise, followed by isopropyl alcohol (ratio of cellulose :isopropanol=1: 30.62) and mixed for 1 hour at 27°C. The carboxylation process was then resumed with monochloroacetic acid in cellulose and MCA of 1 :1.19 ratios and stirred at 55°C for 3 hours before filtering. The filtrated solid was then steeped in methanol at a 50-fold concentration of the pulp used for 24 hours before being neutralized with acetic acid and filtered. CMC was washed with 70% and 96% ethanol to eliminate by-products. CMC was dried at 60°C for 24 hours. CMC was ground to produce CMC powder.

2.5 Production of MCC

OPEFB cellulose was hydrolyzed using a 2.5 N HCl solution at 100°C ± 2°C for 45 minutes, with a cellulose to HCl solution ratio of 1:30. The resulting MCC was filtered and washed with distilled water until neutral. The MCC was then dried at 60°C for 24 hours and ground into a fine powder.

2.6 Production of hydrogel film

The NaOH/urea/water solution was made by dissolving the ingredients in a 100 mL solution at a ratio of 6/4/90. Subsequently, a 3% MCC solution was prepared using the solvent, which was then centrifuged for 10 minutes at 4000 rpm after being stirred for 2 hours at room temperature, frozen for 18 hours, and thawed. The result was a clear solution. Similarly, CMC was made into a 3% solution by dissolving it in distilled water. CMC and MCC solutions were formulated according to CMC and MCC formulations, and glycerol added as much as 10% of CMC/MCC (v/v), then mixed at room temperature (25°C) for 2 hours. The cross-linking process was carried out by adding citric acid to the formulation as much as according to the treatment variation (w/w) and stirring for 2 hours at 30ºC then freeze-thaw for 18 hours and in casting/mold and dried at 80ºC 24 hours.

2.7 Experimental design

The hydrogel film was synthesized by combining CMC and MCC at six different ratios: 100:0, 90:10, 80:20, 70:30, 60:40, and 50:50. Citric acid was used as the crosslinker at three concentrations: 5%, 7.5%, and 10%. The crosslinking process involved material dissolution, freezing-thawing, the addition of a crosslinker to the material formulation, freezing-thawing of formula, molding, and curing at 80°C for 24 hours.

2.8 Characterization of hydrogel film

The hydrogel films obtained were analyzed including moisture content, swelling, tensile strength, and F at strain of max of hydrogel was determined using an ASTM D882 by universal tensile machine, and water vapor permeability.

2.8.1 Swelling

The weighted hydrogel mass is immersed in the swelling medium of aquades pH 7 ± 0.5; during 24 h, the swollen gel is wiped with filter paper, removed, and then immediately weighed. The swelling is calculated using the following Eq. (1).

$$Swelling \ (\%) = \frac{Ws}{Wt} \ x \ 100\% \qquad (1)$$

where Ws is the weight of the swelling hydrogel, and Wt is the dry weight of the hydrogel.

2.8.2 Water vapor permeability

The water vapor permeability was assessed in accordance with ASTM E96M at a temperature of 25°C. Initially, a sample was placed to cover a 50 mL test cup containing 20 mL of water at 100% relative humidity. The initial weight was recorded, followed by the placement of the test cup in a desiccator filled with anhydrous silica at 0% relative humidity. Weight measurements were taken every 4 hours for 24 hours until a constant weight was achieved. The water vapor permeability (WVP) in units of $g.m^{-1}.s^{-1}.Pa^{-1}$ was then calculated using Eq. (2).

$$WVP = \frac{\left(\frac{\Delta m}{\Delta T}\right) x \ T}{A \ x \ \Delta P} \qquad (2)$$

where :
$\frac{\Delta m}{\Delta T}$ = test cup weight per time period
T = film thickness (m)

A   = the area of exposed film
AP   = vapor pressure difference on 2 sides of the film (Pa), 26.4 mmHg = 3519.711 Pa

2.9 Data analysis

Quantitative data were evaluated using analysis of variance (ANOVA) at α 5% significance level (α = 0.05). Significant treatment effects were further analyzed with the Duncan Multiple Range Test (DMRT). The analysis was conducted using IBM SPSS Statistics version 24.

3 Result and Discussion

Hydrogel film was synthesized using MCC and CMC obtained from OPEFB. CMC is the material that acts as the backbone of this hydrogel film structure, which will affect the absorptivity of water and moisture and structurally affect the hydrogel film's elasticity level. In hydrogel synthesis, CMC cannot stand alone in getting hydrogel characteristics with a good water absorption rate; it can also have high mechanical characteristics. Therefore, adding MCC acts as a filler to increase the mechanical strength of the hydrogel. The right proportion of MCC to CMC is needed to obtain high water absorption characteristics while maintaining its mechanical strength.

Crosslinkers play a crucial role in synthesizing hydrogel films by creating crosslinks, which enable the hydrogel to retain absorbed water without dissolving. A network of 3D covalent bonds is required during gelation to obtain a stable cellulose hydrogel structure, and the crosslinking process can facilitate this. Crosslinking will be crucial in producing the desired hydrogel with good absorption properties and high mechanical strength.

The chemical crosslink is permanent, whereas the physical crosslink is reversible, allowing the hydrogel to dissolve easily in response to pH, temperature, and ionic strength changes. This study examined the combination of chemical crosslinking by determining the appropriate concentration of citric acid as the crosslinking agent and physical crosslinking by testing the freeze-thaw and heating stages to establish the optimum conditions for producing robust hydrogels.
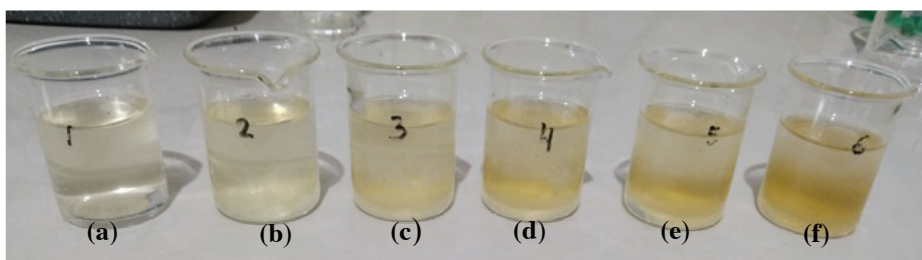

Fig.1. Formulation of CMC: MCC in hydrogel synthesis a) 100 : 0, b) 90: 10, c) 80: 20, d) 70: 30, e) 60: 40 and f) 50: 50

The formulations used in the synthesis of hydrogel film were CMC: MCC with sequential proportions of 100: 0, 90: 10, 80: 20, 70: 30, 60: 40, and 50: 50 with citric acid concentration as a crosslinker of 5%, 7.5% and 10% b/v based on the volume of CMC and MCC formula. Citric acid was added as a solid in the formulation, and the crosslinking process was carried out by stirring for 2 hours at room temperature. Figure 1 shows the sequence of the series of CMC and MCC formulations. The higher the proportion of MCC, the more turbid the color, while the solution containing only CMC gives a clear transparent color.

Citric acid can form ester bonds, which are formed between hydroxyl and carboxyl groups. In this instance, the hydroxyl group of cellulose and the carboxyl group of citric acid will form an ester bond [12,13]. However, if the formula contains glycerol, the bond will first occur with the hydroxyl group of glycerol [14]. Similarly, if no citric acid ester bonds are formed with cellulose, strong hydrogen bonds can be formed between citric acid and cellulose. Therefore, more citric acid tends to give a stiffer and harder structure.

Each hydrogel formulation containing citric acid undergoes crosslinking by being frozen for 18 hours. Following freezing and thawing to room temperature, the hydrogel's mechanical structure is reinforced by casting it at 80°C for 24 hours. Figure 2 illustrates the appearance of the hydrogel solution after the freeze-thaw process. The hydrogel changes from a clear, transparent color to white during the crosslinking process using citric acid.
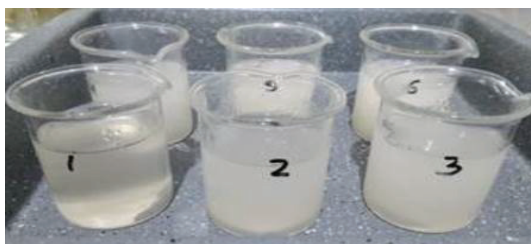

Fig.2. Hydrogel solution after freeze-thaw process

The solutions were cast in a petri dish with a diameter of 5 cm at a temperature of 80°C for 24 hours, or until a film formed. The characteristics of each CMC/MCC formulation can vary from flexible and ductile to brittle, making them prone to breakage when removed from the petri dish. A brittle hydrogel structure is produced when the ratio of MCC to CMC is higher because the crystalline structure of MCC reduces its ability to cross-link. Figure 3 illustrates the hydrogel films from treatments with ratios of CMC: MCC of 90:10 and 80:20.
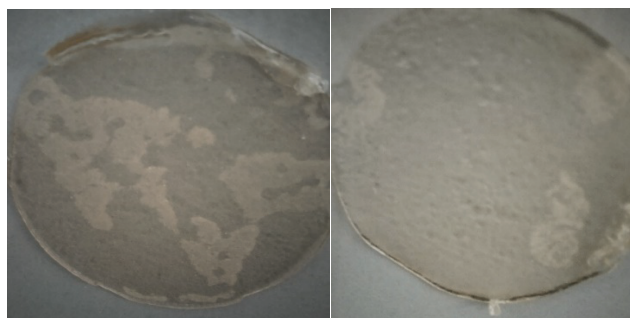

Fig.3. Hydrogel film a) CMC:MCC 90:10 and b) CMC:MCC 80:20

The use of 100% carboxymethyl cellulose (CMC) results in a hydrogel film that is elastic but prone to tearing. When the proportion of microcrystalline cellulose (MCC) is increased to 50%, the hydrogels become less elastic, transitioning from ductile to brittle. Additionally, raising the concentration of citric acid tends to produce hydrogel films that are increasingly resilient and hard, while significantly reducing elasticity. This is evident when the hydrogel film is removed from the petri dish, as it can be challenging to detach. Incorporating citric acid as a crosslinking agent leads to connections forming between the molecules in the CMC and MCC mixture. A higher degree of crosslinking results in a denser network structure,

which restricts the mobility of the polymer chains. Consequently, materials with a greater degree of crosslinking tend to exhibit increased rigidity [15].

The polymer solution crystallizes during freezing, resulting in a physical crosslink reaction. Hydrogen bonding results from the polymer chain's hydroxyl groups interacting with water molecules. The formation of crystals that serve as crosslink sites between polymer chains is induced by freezing the polymer solution. The polymer chains will become more flexible throughout thawing, regaining their freedom. Developing a three-dimensional matrix structure, which traps the solvent in the matrix to form a gel, is the fundamental step in the polymer chain crosslink process [16]. A three-dimensional matrix forms hydrogen bonds through intramolecular and intermolecular bonding, facilitated by hydrophilic functional groups such as -OH, -COOH, and -NH2 groups. The more hydrophilic functional groups present in a polymer, the more likely hydrogen bonds will form.

3.1 Water content of hydrogel film

During the casting process, the hydrogel undergoes a final crosslinking process that involves heating it to 80°C for 24 hours. This results in a non-mushy texture and the formation of an elastic to brittle film layer, depending on the concentration of citric acid and the ratio of CMC and MCC.

Table 1. The water content of hydrogel film

CMC:MCC	Conc.of citric acid (%)			Mean
	5	7.5	10	
100:0	7.36±0.01	8.61±0.96	8.64±0.56	8.20^a±0.20
90:10	9.28±3.53	9.39±0.58	9.13±0.74	9.26^{ab}±1.61
80:20	11.70 ±3.99	10.79±2.02	10.45±1.17	10.97^{bc}±2.16
70:30	12.83±4.38	11.01±1.95	10.75±0.98	11.54^{bc}±2.42
60:40	13.32±0.71	12.07±2.06	11.72 0.51	12.37^c±1.25
50:50	18.56±2.05	10.19±0.23	10.39±0.66	13.04^d±4.38
Mean	12.18±4.27^b	10.34±1.61^a	10.17±1.22^a	

Note: different letters in the same raw and column indicate significantly different treatments (p≤0.05)

Table 1 illustrates that increasing the proportion of microcrystalline cellulose (MCC) relative to carboxymethyl cellulose (CMC) by up to 50% leads to an increase in the moisture content of the hydrogel film. In contrast, raising the concentration of citric acid results in a decrease in the moisture content of the hydrogel film. The water contained in the hydrogel film is strongly bound by the crystalline structure of MCC, making it more difficult to release after casting at 80°C. On the other hand, increasing the concentration of citric acid tends to reduce the moisture content of the hydrogel film, which aligns with the increased brittleness observed in the material. Citric acid contributes to a higher total solid content in the composite, thereby lowering its water content. The hydrogel is designed to absorb and retain water while effectively maintaining its structure. It comprises CMC, which is highly soluble in water, and MCC, which serves as a filler that reduces the hydrogel's solubility in water while still ensuring substantial water absorption. Notably, MCC is a cellulose derivative that is insoluble in both water and alcohol.

3.2 Swelling of hydrogel film

Three different pH values were used to test the swelling power of the hydrogels: neutral (pH 7), acidic (pH 4), and alkaline (pH 10). Under alkaline conditions, specifically at pH 10, the hydrogels in all treatments dissolved completely. In contrast, swelling in acidic conditions (pH 4) was less pronounced than that observed at neutral pH. This aligns with the properties of cellulose-based materials, which tend to swell and dissolve in alkaline environments. In the preparation of hydrogels, MCC is dissolved in a NaOH-urea ionic solution. Additionally, during the synthesis process of CMC, cellulose is macerated with an isopropanol-NaOH solution. This allows NaOH to penetrate and swell the cellulose structure, facilitating the binding of monochloroacetic acid. Consequently, the high pH levels at 10 lead to the complete dissolution of the hydrogel films. The swelling data for the hydrogel films is presented in Table 2.

The analysis of variance (ANOVA) indicated that the proportions of CMC to MCC and the concentration of citric acid significantly affected the swelling ability of the hydrogel film at both neutral pH and pH 4. Under neutral pH conditions, the highest swelling was observed with a CMC to MCC ratio of 80:20 and a 5% citric acid concentration, although the gel deteriorated. In contrast, at pH 4, the greatest swelling occurred with a CMC to MCC ratio of 90:10, also with a 5% citric acid concentration.

The gel began to dissolve at the CMC: MCC ratio of 70:30 with a 5% concentration of citric acid. However, at 7.5% and 10% citric acid concentrations, significant solubility was observed at the CMC: MCC ratio of 50:50. Despite the strong hydrophilic properties of CMC, a hydrogel film with a high water absorption capacity could not be achieved with a 100% concentration of CMC. This suggests that a high absorption rate requires a certain amount of MCC to be effective..

Table 2. Swelling data of hydrogel film at pH 7 and pH 4

Conc. of citric acid (%)	CMC: MCC	*Swelling* (%)			
		pH 7	texture	pH 4	texture
5	100:0	164.70±30.27[b]	gel	151.74±3.44[d]	gel
	90:10	322.72±9.32[de]	gel	440.35±18.56[f]	gel
	80:20	811.39±66.28[g]	decay	194.42±12.98[e]	gel
	70:30	187.39±65.57[bc]	dissolve	0[a]	dissolve
	60:40	0[a]	dissolve	0[a]	dissolve
	50:50	0[a]	dissolve	0[a]	dissolve
7.5	100:0	175.81±5.36[b]	gel	145.71±7.25[cd]	gel
	90:10	163.48±29.21[b]	gel	146.62±5.91[d]	gel
	80:20	202.22±20.24[bc]	gel	156.69±4.97[d]	gel
	70:30	365.94±17.24[ef]	decay	152.76±0.72[d]	gel
	60:40	173.16±23.47[b]	dissolve	117.81±10.98[b]	gel
	50:50	167.86±56.40[b]	dissolve	0[a]	dissolve
10	100:0	161.38±21.07[b]	gel	140.43±10.04[cd]	gel
	90:10	196.00±36.47[bc]	gel	153.85±8.23[d]	gel
	80:20	297.58±44.88[de]	gel	157.34±6.60[d]	gel
	70:30	261.13±41.64[cd]	gel	149.71±12.12[d]	gel
	60:40	438.90±43.72[f]	decay	129.43±3.54[bc]	gel
	50:50	207.31±0.61[bc]	dissolve	0[a]	dissolve

Note: different letters in the same column indicate significantly different treatments (p≤0.05)

The maximum swelling patterns for each concentration of citric acid crosslinker differ significantly. For instance, the gel exhibits high water absorption while maintaining its structure at a CMC: MCC ratio of 90:10 with 5% citric acid. In contrast, different results are observed at a CMC: MCC ratio of 70:30 with 7.5% citric acid. The gel after immersion at pH 7 is shown in Figure 4. Under acidic conditions (pH 4), the greatest swelling occurs at the CMC: MCC ratio of 90:10 with 5% citric acid, but increasing the MCC content to 50% can lead to the dissolution of the gel. At a 5% citric acid concentration, the gel fully dissolves at a CMC: MCC ratio of 70:30, while concentrations of 7.5% and 10% citric acid dissolve at a ratio of 50:50 CMC: MCC. The swelling rate at pH 4 does not show significant differences across these conditions.
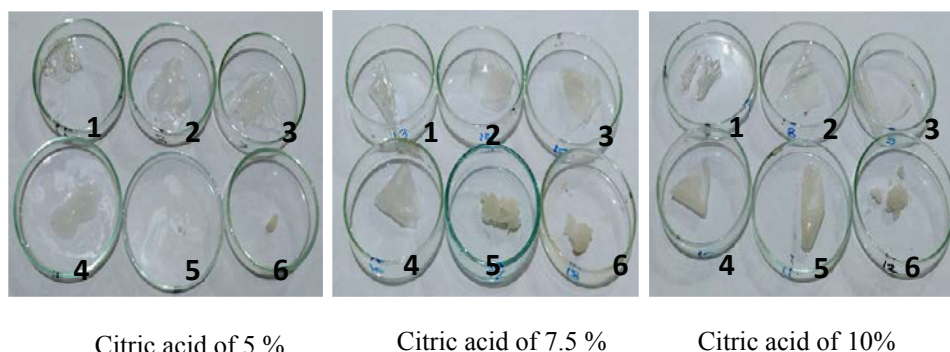

Citric acid of 5 %   Citric acid of 7.5 %   Citric acid of 10%

Fig.4. Hydrogel after immersion in pH neutral (pH 7)

Naturally, the process has increased the crosslinks of CMC-MCC base hydrogels when examining the effects of a single cycle of freeze-thaw and 80°C casting on crosslinks. According to certain research, multiple freeze-thaw cycles are required to achieve the desired swelling and mechanical strength. PVA/n-HA/HACC/freeze-thaw 3-cycle formula still has a low swelling level [17]; PVA/GLE with freeze-thaw 4 cycle swelling level 207% [18]. In the PVA/CH/AgNPs freeze-thaw 3 cycle formula, swelling up to 1000% when the CH formula is increased [19].

Previous work pointed out that increasing the number of carboxylic groups will also increase the number of hydrogen bonds in the hydrogel, and increasing -H bonds will reduce solubility [20]. This will certainly increase the amount of water in the hydrogel structure. Carboxylic groups have two effects on water absorption; when the carboxylic group is fully protonated (COOH), it will form many hydrogen bonds that can reduce water absorption in the hydrogel. On the other hand, when ionized (COO-), an electrostatic repulsive force will be produced that can open the gel and increase its absorption ability.

The cross-linking process using citric acid is thought to occur through crosslinking specifically to the hydroxyl groups at C2 or C3 of adjacent anhydroglucose units. Citric acid carboxyl molecules can connect it. The results showed significant swelling at 5% citric acid concentration; increasing citric acid concentration to 10% showed no significant change. Therefore, further addition of citric acid did not show a considerable increase in the ability of the hydrogel to trap the maximum amount of water. The denser the crosslinks in the hydrogel film, the less flexibility to expand [21]. This is related to the low water trapping ability, thus lowering the swelling rate. Similarly, swelling is higher in neutral water than in ionic or buffer solutions.

The hydrogel film formed contains hydrogen bonds between the hydroxyl groups of cellulose and crosslinks created by citric acid ester bridges with the cellulose. When the

hydrogel becomes wet, these hydrogen bonds can break, leading to degradation and dissolution. However, the cellulose that has undergone crosslinking can maintain the hydrogel's structure in wet conditions. Ester bonds are stable in water, so when the cellulose is wet, the crosslinks formed through esterification with the hydroxyl groups help prevent the material from swelling and preserve its structure. It is assumed that there is a correlation between the number of crosslinks and the strength of those crosslinks.

In the freeze-thaw method, the crosslinking process begins during the freezing phase and continues for 24 hours at 80°C for curing. Generally, a higher number of crosslinks results in stronger hydrogels. Research conducted earlier highlighted that synthesized cellulose/CMC/PVA-based hydrogels with epichlorohydrin crosslinkers, the formulations of CMC::MCC 90:10 and CMC: MCC 80:20 with 5% citric acid crosslinkers exhibit comparable swelling performance [22]. The highest swelling of cellulose/CMC/PVA was at a ratio of 3/3/4 with swelling of 6.33 g/g, while that of cellulose/CMC/glycerol was at a ratio of 2/4/5 with the highest swelling of 4.65 g/g. Therefore, an effort to synthesize hydrogels with food-grade crosslinker components is quite promising.

3.3 Tensile strength of hydrogel film

The tensile strength test measures the mechanical resistance of hydrogel film to tensile forces or strain. This assessment provides insight into the film's ability to withstand stress without fracturing or deforming. Specifically, a CMC: MCC ratio of MCC 100:0 resulted in the lowest tensile strength, distinguishing it from the other treatments. Additionally, a citric acid concentration of 5% produced the weakest tensile strength, whereas concentrations of 7.5% and 10% showed similar tensile strength levels that were not significantly different from each other.

Table 3. Tensile strength and strain at F max of hydrogel film

Conc. of citric acid (%)	CMC: MCC	*Tensile strength* (MPa)	*Strain at F max* (%)
5	100:0	0.037±2,83E-4	12.83±0.00[ab]
	90:10	0.303±1.02E-2	48.74±2.42[ghi]
	80:20	0.225±1.74E-2	75.99±1.87[j]
	70:30	0.101±5.99E-2	20.85±0.81[abcd]
	60:40	0.254±3.53E-3	8.53±0.00[a]
	50:50	0.500±2.44E-3	10.86±0.32[ab]
7.5	100:0	0.195±7.05E-5	20.37±0.05[iabcd]
	90:10	0.404±9.09E-3	43.13±0.72[efgh]
	80:20	0.532±1.61E-2	60.22±1.88[i]
	70:30	0.542±4.95E-2	57.18±1.31[hi]
	60:40	0.283±2.13E-2	27.74±2.80[bcde]
	50:50	0.515±4.99E-2	4.60±0.13[a]
10	100:0	0.089±3.89E-3	20.82±0.01[abcd]
	90:10	0.328±3.28E-2	30.94±1.46[cdef]
	80:20	0.545±2.40E-2	42.59±1.72[efgh]
	70:30	0.305±2.01E-2	45.27±2.23[fghi]
	60:40	0.221±1.57E-2	31.93±0.57[defg]
	50:50	0.123±8.13E-3	14.41±0.02[abc]

Note: different letters in the same column indicate significantly different treatments (p≤0.05)

The tensile strength of hydrogel film is detailed in Table 3. At a 5% citric acid concentration, the tensile strength of the 80:20 ratio is lower than that of the 90:10 ratio, while the strain at maximum force (Strain at F max) is at its highest. Tensile strength and strain in the CMC: MCC 80:20 and 70:30 treatments were fairly balanced at 7.5% citric acid. When the citric acid concentration is 10% as a crosslinker agent, the strain at the maximum force is smaller. This indicates the elasticity of each hydrogel film treatment when pulled. The treatment of CMC: MCC 80:20 with citric acid 5% will give more elasticity than the others, as well as the same treatment with citric acid 7.5%.

While some treatments have a lower strain at F max, others have a higher tensile strength. Weakly linked chains are thought to cause some chain fractures, whereas strong crosslinks allow chains to control the tensile strength and elasticity properties of hydrogels during deformation. Furthermore, several hydrogen bonds at the molecular scale combine freeze and casting effects, aggregation, and strong crosslinks [23].

3.4 Water vapor permeability of hydrogel film

The measurement of water vapor diffusion through the hydrogel film is expressed in terms of water vapor permeability (g/s·m·Pa), which accounts for the amount of water vapor that passes per unit area, time, and pressure gradient. This process involves two main factors related to gas interaction with the polymer material: the morphology of the polymer, including its pores or cracks, and the solubility-diffusion effects (gas solubility). Table 4 shows that the hydrogel film composed of CMC and MCC in an 80:20 ratio exhibits higher water vapor permeability at both 5% and 7.5% citric acid concentrations. Increasing the percentage of MCC at any given citric acid concentration results in reduced permeability to water vapor. Additionally, the permeability for the same CMC: MCC treatment is higher at the 5% citric acid concentration compared to the 7.5% concentration. This variation is believed to be influenced by the density of the hydrogel; at 7.5% citric acid concentration, the hydrogel tends to assume a more ductile structure. This observation is consistent with the tensile strength data presented in Table 3, which indicates that the 7.5% citric acid concentration yields greater tensile strength.

Table 4. Water vapor permeability (g/m.Pa.24h) of hydrogel film

CMC:MCC	Conc.of citric acid (%)		
	5	7.5	10
100:0	-	-	-
90:10	3.662×10^{-5}	3.079×10^{-5}	3.397×10^{-5}
80:20	3.688×10^{-5}	3.434×10^{-5}	2.831×10^{-5}
70:30	3.422×10^{-5}	2.806×10^{-5}	2.823×10^{-5}
60:40	-	-	2.361×10^{-5}
50:50	-	-	-

Note: - not measurable

The significant decrease in water vapor permeability can be attributed mainly to adding a citric acid crosslinker. The esterification reaction grafts hydrophobic groups (esters) on the starch chains, contributing to lower water vapor permeability as these hydrophobic groups hinder the diffusion of water vapor molecules through the matrix [24]. Crosslinks in the stronger hydrogel film will provide a denser structure inside, and this will correlate with a

decrease in the permeability of the hydrogel film to water vapor. Hydrogen bonding will reduce the diffusion ability of gases and liquids in the hydrogel film.

Hydrogel films designed for wrapping fresh fruit products should effectively preserve the product's moisture to ensure its freshness. They need to be able to absorb water vapor from respiration to prevent the fruit from losing excessive water and to maintain a balanced level of moisture within the product. When used for wrapping, the hydrogel film must be pliable, durable, and resistant to tearing, making its mechanical strength a crucial consideration.

4 Conclusion

The hydrogel film can effectively preserve fresh products by absorbing water vapor and maintaining the product's moisture equilibrium conditions within its matrix. With a 5% concentration of citric acid as a crosslinker, the CMC/MCC 90:10 treated hydrogel film demonstrates good water absorption and maintains a strong mechanical structure. According to the formula, the hydrogel film has enough flexibility and stretchiness to wrap around products. Likewise, its ability to let water vapor pass through is expected to maintain the moisture content of the fresh product.

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References

1. D. Klemm, B. Heublein, H. P. Fink, and A. Bohn, Angewandte Chemie - International Edition **44**, 3358 (2005)
2. S. Dacrory, H. Abou-Yousef, R. E. Abou-Zeid, S. Kamel, M. S. Abdel-Aziz, and M. Elbadry, Journal of Renewable Materials **6**, 536 (2018)
3. K. Varaprasad, G. M. Raghavendra, T. Jayaramudu, M. M. Yallapu, and R. Sadiku, Materials Science and Engineering C **79**, 958 (2017)
4. A. Sannino, C. Demitri, and M. Madaghiele, 353 (2009)
5. E. Marsano, E. Bianchi, and L. Sciutto, Polymer **44**, 6835 (2003)
6. Y. Zhao, M. He, L. Zhao, S. Wang, Y. Li, L. Gan, M. Li, L. Xu, P. R. Chang, D. P. Anderson, and Y. Chen, ACS Applied Materials and Interfaces **8**, 2781 (2016)
7. M. A. Raza, J.-O. Jeong, and S. H. Park, Frontiers in Materials **8**, 1 (2021)
8. R. Salihu, S. I. Abd Razak, N. Ahmad Zawawi, M. Rafiq Abdul Kadir, N. Izzah Ismail, N. Jusoh, M. Riduan Mohamad, and N. Hasraf Mat Nayan, European Polymer Journal **146**, 110271 (2021)
9. N. Roy, N. Saha, T. Kitano, and P. Saha, Carbohydrate Polymers **89**, 346 (2012)
10. S. Susi, M. Ainuri, W. Wagiman, and M. A. F. Fallah, International Journal of Biomaterials **2023**, 1 (2023)

11. D. M. Parid, A. S. Baharuddin, M. A. P. Mohammed, A. M. Johari, S. Zubaidah, and A. Razak, **13**, 535 (2018)
12. E. Chabrat, H. Abdillahi, A. Rouilly, and L. Rigal, Industrial Crops & Products **37**, 238 (2012)
13. N. Wang, X. Zhang, N. Han, and S. Bai, Carbohydrate Polymers **76**, 68 (2009)
14. B. H. Zhang, Z. Wang, Z. Zhang, J. Wu, J. Zhang, and J. He, 698 (2007)
15. S. Rimdusit, K. Somsaeng, P. Kewsuwan, C. Jubsilp, and S. Tiptipakorn, Engineering Journal **16**, 15 (2012)
16. J. S. Kim, Y. Y. Lee, and T. H. Kim, Bioresource Technology **199**, 42 (2016)
17. S. Gan, W. Lin, Y. Zou, B. Xu, X. Zhang, J. Zhao, and J. Rong, Carbohydrate Polymers **229**, (2020)
18. W. X. Waresindo, H. R. Luthfianti, D. Edikresnha, T. Suciati, F. A. Noor, and K. Khairurrijal, RSC Advances **11**, 30156 (2021)
19. A. Kumar, T. Behl, and S. Chadha, International Journal of Biological Macromolecules **149**, 1262 (2020)
20. R. Barbucci, A. Magnani, and M. Consumi, Macromolecules **33**, 7475 (2000)
21. D. Kundu and T. Banerjee, Heliyon **6**, e03027 (2020)
22. B. N. Mohamed, S. F. Chin, and M. E. Wasli, **34**, 53 (2023)
23. X. Guo, X. Dong, G. Zou, H. Gao, and W. Zhai, Science Advances **9**, 1 (2023)
24. F. D. Martinez-Garcia, T. Fischer, A. Hayn, C. T. Mierke, J. K. Burgess, and M. C. Harmsen, Gels **8**, 1 (2022)