Physical Evaluation of PVA/Chitosan Film Blends with Glycerine and Calcium Chloride

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Abstract. PVA/chitosan film has been fabricated by using drop casting method. PVA/chitosan film is produced by dissolving 2% (w/v) PVA solution and 2% (w/v) chitosan solution. PVA/chitosan film is produced with weight ratio variation (w/w) 100/0, 75/25, 50/50 and 0/100. The film is fabricated using drop casting method in Petry dish with diameter 11 cm at room temperature and RH 50%–60% during seven days. The mechanical properties were characterized by using Universal Technical Machine (UTM) and UV-Vis to understand the physical properties of weight ratio (w/w) of PVA/Chitosan film by addition of plasticizer and calcium chloride. The film thickness tends to decrease with PVA content. The addition of chitosan will increase film thickness, and it will decrease swelling index, elongation (%), and transmittance of UV rays. The additions of plasticizer to PVA/Chitosan film will increase film thickness and elongation (%), and it will decrease swelling index, tensile strength and transmittance of UV rays. The crosslink of PVA/Chitosan film with calcium chloride will decrease film thickness, swelling index, elongation (%) and transmittance of UV rays, and increase tensile strength.

Keywords: chitosan, PVA, Drop casting, plasticizer, calcium chloride

1. Introduction
In the few years, development of food packaging with the antibacterial system has been increased. It could happen because of the consumer response and modern trend by produced the healthy and fresh food. The research was focused on the development of biopolymer film which is safe for health and environment. The biopolymer film was used as synthetic food packaging which is antibacterial and environment-friendly. This film was investigated to know the capability of keeping the food longer and increased the quality of food by avoided vapor movement, oxygen, and fat [1]. Biopolymer film was investigated by using a polymer with protein and polysaccharide, for example, chitosan, cellulose and cassava flour [2]. Chitosan is a synthetic polymer with antibacterial properties [3]. Chitosan was blended with other material for increasing the mechanical properties. Addition of PVA into Chitosan polymer was investigated. It showed the decreasing of UV transmittance which is given antibacterial properties [4]. Chitosan was added by silica and PEG to increased mechanical properties [5].

PVA is a polymer with low toxicity, biocompatible, hydrophilic, chemically stable and easy to fabricate [5]. PVA and Chitosan blends were developed and characterized in biology application. The film was accessible to biodegradable, and antioxidant by mixing PVA and Chitosan with different weight ratio [2]. Addition of chitosan into PVA solution will be decreasing mechanical strain of film. It will be increasing the mechanical stiffness of film [4]. The chemical synthesis between chitosan and PVA could be improved in mechanical strength thermal stability and swelling capability in chitosan film [6]. Addition of glycerin into PVA will be decreased transition temperature and thermal decay [7].

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Modified PVA by addition of glycerin made tensile film decrease, but the elongation at break is higher. PVA/chitosan could be modified by added another material or fabricated by other methods. The purpose of modification in mechanical and optic properties to the blend film will be applicable. Modification by addition of calcium chloride to chitosan will be an influence to decreased the depreciation mass of tomatoes and extend the age of tomatoes 5-8 days longer than control sample [7]. The film decreases by the addition of calcium chloride to sodium alginate solution [8].

In these research, PVA/Chitosan film was made by drop casting method. The weight ratio of PVA/chitosan will be made by addition with glycerin and calcium chloride. The film will be characterized by UTM and UV vis spectroscopy. The prospect of the film for food packaging will be investigated by test the film with fresh vegetable.

2. Experimental Procedure

2.1 Materials

In conducting this research, chitosan medium molecular weight with deacetylation percentage (DD) of 75-85% deacetylated, and poly(vinyl alcohol) (PVA) molecular weight 89.000-98.000 (+99% degree hydrolysis) were purchased from Sigma Aldrich (St.Louis, MO, USA). The solvent of chitosan was 98% acetic acid which purchased from a local company of PT.Brataco (Indonesia). Glycerol and calcium chloride provided by Sigma Aldrich, respectively.

2.2 Preparation of film

Preparation of PVA/Chitosan with glycerine: The chitosan was soluble acid thus a blend of chitosan solution 2% was prepared by dissolving chitosan in acetic acid 2wt%. After stirring and heating at 80°C during 5 hours, chitosan 2wt% was mixed with PVA 2wt% solution and stirred for 4 hours at 60°C until producing a homogeneous solution. The weight ratio for PVA/chitosan was 100/0, 75/25, 50/50 and 0/100. Glycerin 10% (w/w) from chitosan mass was added. The solution was stirred for one hour at 70°C.

Preparation of PVA/Chitosan with calcium chloride: PVA/chitosan at 75/25 before addition of glycerin was dropped in Petri dish by drop casting method. This film was put in 1 % (w/v) calcium chloride in ethanol solution. The solution with the film was stirred for 30-40 minute at room temperature.

Characterization: Mechanical characterization was used Universal Testing Machine (UTM) ZWICK/ZOS. The output of this characterization included thickness, strain, and stress. Optical characterization was used UV-visible spectrometer SHIMADZU UV-1700.

3. Result and Discussion

Mechanical Properties

Table 3.1 shows the thickness of film with a different weight ratio of PVA/Chitosan and by addition of glycerine and calcium chloride. PVA without the addition of chitosan shows that decreasing of thickness. PVA/chitosan blend shows the increasing in thickness rather than PVA 100%. The thickness will be increasing by addition chitosan. Chitosan 100% shows the thickest film. The increase in thickness will decrease by addition PVA because the thickness of film depends on PVA composition. Chitosan was a positive charge, and it has wide hydration film. Chitosan could hold water molecule that could avoid polymer chain and produce the thick film. When PVA concentration increased, the thickness will be decreasing.
Table 3.1 Thickness (a) and wide (A)

| Weight ratio      | a (mm) | A (mm²) | Uₐ (mm²) |
|-------------------|--------|---------|----------|
| 50/50             | 0.029  | 0.145   | 0.029428 |
| 75/25             | 0.038  | 0.19    | 0.038328 |
| PVA 100%          | 0.016  | 0.08    | 0.016763 |
| 75/25 + glycerin  | 0.056  | 0.28    | 0.056223 |
| 75/25 (0.1 gr/10 ml) | 0.025 | 0.125 | 0.025495 |
| 75/25 (0.2 gr/20 ml) | 0.021 | 0.105 | 0.021587 |
| 75/25 (0.3 gr/30 ml) | 0.022 | 0.11 | 0.022561 |

Addition glycerin will influence the polymer film. Also, glycerin will be increased the thickness of the film. It is caused by hygroscopic properties of glycerin. Hygroscopicity is the capability for attracting and the bond water molecule in the air by absorption process. This property allows glycerin to attract water molecule from the air to the film. Water molecule will be attached and soak in the polymer film. Addition glycerin will increase the thickness of the film. Decreasing in thickness by adding calcium chloride is caused by breaking in function chain of PVA/Chitosan film because of the reaction of calcium chloride [8]. The decreasing of thickness is caused translation of positive charge. Calcium chloride is solved in ethanol. It forms calcium ion and chloride ion. The result is electrolyte concentration in solution will be increased. The film thickness became decreased.

Table 3.2 Stress

| Weight ratio      | Σ (MPa) | Uσ (MPa) |
|-------------------|---------|----------|
| 50/50             | 12.26   | 2.488    |
| 75/25             | 22.00   | 4.438    |
| PVA 100%          | 17.44   | 3.655    |
| 75/25 + glycerin  | 4.84    | 0.973    |
| 75/25 (0.1 gr/10 ml) | 26.10 | 5.125    |
| 75/25 (0.2 gr/20 ml) | 12.41 | 2.552    |
| 75/25 (0.3 gr/30 ml) | 33.53 | 6.877    |

PVA/chitosan blend film has high stress than pure chitosan film [2]. There is an interaction between PVA and chitosan molecules. This interaction will increase mechanical strength from PVA/chitosan blend film. The increasing of mechanical strength from PVA/chitosan film because of the interaction between –OH and NH₂ of both polymer [9].

Pure PVA has the higher strain (ε). Also PVA into the blend, the flexibility of film will be increased [2]. Addition of glycerin will be decreased intermolecular force between PVA and chitosan. It causes the distance between PVA and chitosan wider and sprawl. The film blend will be comfortable to be broken when the force was given. By the addition of plasticizer (glycerin), the strain became increasing [10]. Glycerin cause is decreasing intermolecular force between PVA and chitosan. Decreasing of intermolecular force will increase the flexibility of blend film. Addition of calcium
chloride will influence the strain and stress of blend film. The strain indicates the formation of between carboxyl group in the interface of PVA with Ca$^{2+}$ from calcium chloride [8; 11]. The increasing of calcium ion ((Ca$^{2+}$)) will decrease the strain of film.

| Weight ratio  | $\varepsilon$ (%) | $U\varepsilon$ (%) |
|---------------|-------------------|-------------------|
| 50/50         | 13.32             | 2.018             |
| 75/25         | 49.155            | 2.229             |
| PVA 100%      | 61.67             | 2.350             |
| 75/25 with glycerin | 53.60           | 2.270             |
| 75/25 crosslink 0,1 gr/10 ml | 15.55            | 2.024             |
| 75/25 crosslink 0,2 gr/20 ml | 2.704            | 2.001             |
| 75/25 crosslink 0,3 gr/30 ml | 22.22            | 2.049             |

**Figure 1.** Transmittance spectrum of PVA/chitosan film

Picture 1 shows that pure PVA has the higher transmittance spectrum than another blend. It is at 60% - 90%. By the addition of chitosan, the transmittance spectrum will decrease. Transmittance spectrum is the capability to protect the film. The transmittance spectrum is related to the sum of radiation energy that could penetrate the film. The high transmittance spectrum shows the high radiation energy to penetrate the film.

**Figure 2.** Transmittance spectrum of modified PVA/chitosan film
Picture 2 shows the PVA/chitosan 75/25 has the highest transmittance spectrum at 30% - 90%. After addition of calcium chloride, the transmittance spectrum continues to decrease and constant at wavelength 250 nm. By the addition of glycerin, the transmittance decrease but not stable. The low spectrum transmittance shows capability to protect the radiation. Picture 2 shows that modified PVA/chitosan with calcium chloride could resist the radiation.

4. CONCLUSION

The weight ratio of PVA/chitosan will influence the physical properties of blend film. Domination of PVA concentration will increase the swelling, spectrum transmittance, strain and stress of the blend film. Addition of plasticizer and crosslink with calcium chloride will decrease the swelling, transmittance spectrum, and stress of blend film.

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