Improving Properties of Arrowroot Starch (*Maranta arundinacea*)/PVA Blend Films by Using Citric Acid as Cross-linking Agent

Enny Sholichah\(^1\,^2\), Bambang Purwono\(^2\), Pramono Nugroho\(^1\)

\(^1\)Development Centre of Appropriate Technology Indonesian Institute of Sciences, Jl. KS. Tubun No. 5 Subang West Java, Indonesia, 41213
\(^2\)Department of Chemistry, Faculty of Mathematics and Sciences Universitas Gadjah Mada, Sekip Utara Bulaksumur Yogyakarta Indonesia, 55281

E-mail address: enny.sh002@gmail.com

**Abstract.** This research studied the effect of PVA as organic polymer and citric acid as crosslinker agent in the arrowroot starch/PVA blend films. The properties of films were investigated by water uptake, water vapor permeability, mechanical properties, thermal stability, spectra of FTIR and XRD patterns. PVA used in this research influenced the film properties at the highest concentration. The cross-linkingsinter or intra molecules of arrowroot and PVA were developed as ester bonds which are formed from the reaction of hydroxyl groups consisting of starch and PVA with citric acid. The ester bond was confirmed by FTIR spectra. The increase of the amount of citric acid affected significantly on physical, chemical and mechanical properties, water uptake, WVP and crystallinity. Water barrier level was reduced by decreasing of water uptake and WVP succeeded significantly with increased crosslinking. Cross-linking impact the thermal stability of the films. The elasticity of the films also increases the production of citric acid as a plasticizer in the making of the films as a food packaging material.

1. **Introduction**

Tubers starch is a potential carbohydrate as the material of film preparation because of their capability forming a good film and its abundance in every region [1–5]. Starch consists two main components they are linear polymer defined as amylose and branched polymer known as amylopectin [6]. Yulianti and Ginting [7] have made edible film using various type of tubers starch there were cassava, sweet potato, ganyong (*Canna edulis*) and arrowroot. They have found that the arrowroot film was the best mechanical properties. The weakness of the starch edible film is having high water vapor transmission rate because starch is hydrocolloid material has many hydroxyl groups which can make the hydrogen bonds with water molecules [8].

Modification process is required to improve the performance of starch edible film to implement it as food packaging material to improve the quality and shelf life of the product. Cross-linking modification on starch was done to produce a better thermal stability, mechanical properties and water resistance characteristic [9–12]. Furthermore, blending starch with organic polymer like polyvinyl alcohol (PVA) and cross-linking modification in film preparation was used by Negim et al. [13] and Liu et al. [14] to improve the quality of film especially in water barrier function. PVA is widely used for food packaging ingredient because it has good stability on oil or lipid, tensile strength, high elasticity [15–17] and biodegradable polymer [13,18].

Ether or ester bond is a covalent bond between linear or branched polymer that formed in a cross-linking process. Cross-linking modification gains the degree of polymerization and molecular mass, and also decrease the water solubility [19]. Many compounds can be applied as the cross-linker agents such as citric acid, sodium trimetaphosphat, sodium tripoliposphat, epichlorohydrin, glutaraldehid, sodium tetraborat, dan POCl\(_3\) [9], [14], and [20].
In our present work, citric acid was used as the crosslinker agent for arrowroot starch and PVA in film preparation. Citric acid was chosen because it shows high effectivity as a crosslinker agent at a low level. The other advantage is citric acid has lower hazardous level than glutaraldehyde, epicholohydrin and sodium hypophosphite [9]. The effect of concentration of PVA and citric acid on the physical and mechanical properties, water uptake, water vapor permeability, thermal stability and the structure of film matrix has been studied.

2. Experimental method

2.1. Materials

Arrowroot starch was obtained from UKM Sukabumi Yogyakarta, Polyvinyl alcohol (PVA) fully hydrolyzed was produced by Sigma Aldrich and citric acid by Merck.

2.2. Procedures

2.2.1. Film preparation

Arrowroot starch solution (5%) was heated and stirred until gelatinized (T: ± 70 °C), then citric acid was added. Heating and stirring were continuously proceeded at 80 °C for 10 minutes. This mix was called solution A. Solution B was prepared by dissolving PVA in water, heated and stirred until perfectly dissolved. Subsequently, citric acid was added into PVA solution. This mix was heated and stirred at 80 °C for 10 minutes. The amount of citric acid in both solutions was same. The Solution A and B were mixed at 80 °C for 10 minutes. At the end, the final solution was poured into Petri-dish and dried in the oven dryer at 50 °C. The films were stored in the tight plastic box at room temperature for at least 24 hours before characterization.

| Sample name | Arrowroot Starch (g) | PVA (g) | PVA (%) | Citric acid (g) | Citric acid (%) |
|-------------|----------------------|---------|---------|----------------|----------------|
| P1C1        | 2                    | 0.1     | 0.25    | 0              | 0              |
| P1C2        | 2                    | 0.1     | 0.25    | 0.1            | 0.25           |
| P1C3        | 2                    | 0.1     | 0.25    | 0.2            | 0.50           |
| P1C4        | 2                    | 0.1     | 0.25    | 0.3            | 0.75           |
| P2C1        | 2                    | 0.2     | 0.50    | 0              | 0              |
| P2C2        | 2                    | 0.2     | 0.50    | 0.1            | 0.25           |
| P2C3        | 2                    | 0.2     | 0.50    | 0.2            | 0.50           |
| P2C4        | 2                    | 0.2     | 0.50    | 0.3            | 0.75           |
| P3C1        | 2                    | 0.3     | 0.75    | 0              | 0              |
| P3C2        | 2                    | 0.3     | 0.75    | 0.1            | 0.25           |
| P3C3        | 2                    | 0.3     | 0.75    | 0.2            | 0.50           |
| P3C4        | 2                    | 0.3     | 0.75    | 0.3            | 0.75           |
| P4C1        | 2                    | 0.4     | 1       | 0              | 0              |
| P4C2        | 2                    | 0.4     | 1       | 0.1            | 0.25           |
| P4C3        | 2                    | 0.4     | 1       | 0.2            | 0.50           |
| P4C4        | 2                    | 0.4     | 1       | 0.3            | 0.75           |

The total amount of ingredient was 40g by adding water

2.2.2. Water Vapor Permeability (WVP)

Water vapor permeability of films was determined based on the ASTM E96-00 [17]. The films were sealed on the weighing bottle (diameter ± 2.5cm) filled by silica gel (± 5 g). and then placed in the desiccator where the relative humidity (RH) was controlled at ±78% using saturated solution of NaCl. The weight of the bottles was measured every hour for 7 hours. The weight differences in the interval
2.2.3 Water Uptake
The water uptake of films was measured according to the method described by Setiani et al. [22], the (2x2cm) films were dried in the oven dryer at 100-105 °C for 1 hours, then stored in the desiccator for 30 minutes and weight (initial weight). The next step was deeping the film in the water for 10 seconds, swabbing the remaining water on the film surface and weighing the films. This step was repeated until obtained the constant weight (final weight). The water uptake was calculated by equation (3).

\[
\text{Water uptake} = \frac{\text{Final weight} - \text{Initial weight}}{\text{Initial weight}} \times 100\%
\]

(3)

2.2.4. Mechanical properties
The tensile strength and elongation were measured by using Texture Analyzer Zwick BL-GRS500N in accordance with the ASTM D 882 as used by [22]. The tensile strength and elongation were obtained by calculation using equations (4) dan (5).

\[
\tau = \frac{F_{\text{max}}}{A}
\]

(4)

\[
\text{Elongation (%)} = \frac{d_r}{d_0} \times 100\%
\]

(5)

Where \(\tau\) is tensile strength (MPa); \(F_{\text{max}}\) is the maximum force; \(A\) is the area of film cross-section (mm²); \(d_r\) is the distance of rupture (mm) and \(d_0\) is the distance onset of separation (mm).

2.2.5. Thermal Analysis
Thermal stability of film was analyzed using Linseis–DTA PT1600. Sample (3 mg) was sealed on the aluminum pan and heated at 25 °C - 500 °C which the heating rate was 10°C/min.

2.2.6. Fourier Transform Infra Red (FTIR)
Identification of chemical structure of films modified cross-linking was carried out by FTIR Thermoscientific Nicolet iS-10 in wave number 4000-5000cm⁻¹ and sensitivity 50cm⁻¹[3,23].

2.2.7. X-Ray Diffraction
X-ray diffractometer (RigakuSmartlab) scanned the films at 2θ: 5°- 40°, rate 2°/min. The instrument was set at 30 mA and 40 kV and use x-ray of Cu Kα with \(\lambda\) 1.54˚A. The relative cristalinity was calculated according the equation (6) [24].

\[
\text{Relative cristalinity} = \frac{\text{Cristaline Area}}{\text{Cristaline Area} + \text{Amorhous area}} \times 100\%
\]

(6)

2.2.8. Statistical analysis
The effect of PVA and citric acid in the film properties was determined by Analysis of variance (ANOVA) and post-hoc (Duncan Test, P<0.05) test was performed to find out the difference between the variables. SPSS version 2016 program was employed for Statistical analysis.

3. Result and Discussion
3.1 Water Vapor Permeability (WVP)
WVP is a parameter of film properties that greatly affect the function of film as packaging material to increase the shelf life of food products. High water activity can accelerate the growth of microorganisms
as contaminants that cause damage to a food product. Water vapor permeability describes the movement of water vapor from two different places or systems that are the environment inside and outside the film [25].

![Figure 1. Water vapor permeability of films](image1)

PVA concentrations of less than 0.75% did not significantly influence the WVP but the addition of 0.25% citric acid was able to significantly decrease the WVP. Interaction of both also impact to the decreasing of the WVP of the films. Debeaufort and A. Voilley [25] confirmed that the material composition and film structure may affect the molecular transfer mechanism of water and the way to prevent the entry of water molecules. Citric acid served as in the formation of ester bonds intra and inter molecule starch and PVA caused molecules of starch and PVA increasingly compacted so that blocked the water molecule transfer. Furthermore, the ester bond formed reduces the hydroxyl group on starch and PVA where the hydroxyl groups are the active site of hydrogen bonds. Hydrogen bonding is the interaction between the water molecules and hydroxyl groups of starch and PVA (Figure 2).

![Figure 2. Hydrogen bonding between water molecule and starch](image2)

3.2. Water Uptake
The water uptake determination aimed to characterize the water resistance of the films. The small value of water uptake indicate the better level of the water resistance and vice versa [26].

![Figure 3. Water uptake of films](image3)
The concentration PVA (1%) significantly changed the water uptake but not in PVA 0.25-0.75%. While the increase of citric acid concentration influenced the water uptake of films significantly starts from 0.25%. It means that the higher the concentration of citric acid the smaller the water absorption. This result showed that cross-linking was successful to reduce the water absorption capacity of the film, it was equal with the study of Seligra et al. [23].

![Scheme of cross-linking(a) starch and (b) PVA](image)

**Figure 4.** Scheme of cross-linking(a) starch and (b) PVA

### 3.3. Mechanical properties

Garcia et al. [27] stated that physical, chemical and temperature conditions are able to affect the mechanical properties of the film. Moreover, the interaction between the components of film impact the mechanical properties. Tensile strength is the maximum force given until the film is broken by the width of the cross-section area. While the elongation is the length of the strain until it is broken by the initial length.

![The tensile strength of films](image)

**Figure 5.** The tensile strength of films

The effect of PVA level is described in figure 5, where the concentrations of PVA 0.25-0.75% did not significantly impact the tensile strength of the films. The tensile strength of the film increased with the addition of 1% PVA. This result means that the PVA level less than 1% did not change the tensile strength of the films. It is equal to the results of Rapa et al. [18] and Azahari et al. [28] which the tensile strength of PVA films decreased with increasing amounts of corn starch addition. Gelatinized starch is at amorphous structure so that decreases the tensile strength of the film. Negim et al. [13] and Sadhu et al. [29] reported that every PVA monomer contains a hydroxyl group that can form hydrogen bonds so it is possible to increase the interaction strength in the matrix and produces higher tensile strength.

The use of citric acid as a crosslinking agent at concentrations of 0.5% and 0.75% reduced the tensile strength of the film significantly, this result is similar to [30] and [31]. The amount of citric acid used in film preparation greatly influences the mechanical properties of the film. According to the study of Reddy et al. [9], cross-linking between starch molecules that can increase the molecular weight of starch so that the tensile strength of the films is higher. The addition of citric acid less than 5% (dry basis) affects the increase of tensile strength of the film. According to Menzel et al. [10], the use of citric acid causes two reactions that are cross-linking and hydrolysis. At pH 2, the larger cross-linking as well as the hydrolysis process is indicated by the decreasing of the molecular weight of starch. Therefore, the decrease of tensile strength on the addition of citric acid 0.5 and 0.75% could be affected by the hydrolysis of glycoside bond in starch.
The elongation of the film did not change significantly with the addition of PVA (0.25-1%). The addition of citric acid (0-0.5%) did not significantly also affect the elongation of films. While concentration at 0.75%, the elongation increased significantly. This result is consistent with the study of Negim et al. [13] and Yoo et al. [30]. The hydrolysis reaction of the glycosidic bond in starch decreased the molecular weight of the starch which could increase the mobility of the starch molecules. Furthermore, the hydrolysis reaction also generated the amount of free OH groups that can form hydrogen bonds and proceed greater strain.

![Figure 6. The elongation of film](image)

**3.4. Thermal analysis**

DSC thermogram (Figure 7) shows that non-modified cross-linking film (P1C1) shows an endothermic peak at <100°C which is the temperature of gelatinizing arrowroot starch. These results were consistent with the thermogram of DSC starch arrowroot resulted by the study of Pratiwi [32] where the gelatinized temperature was at 69.17-80.03 °C, likewise Valencia et al [36] obtained the temperature of gelatinization of arrowroot starch is 65.5 ± 0.1°C. Inter and intra molecules interaction between the starch and PVA were developed by cross-linking due to the changes of structure of arrowroot starch so that there is no endothermic peak at that temperature.

Hemalatha [33] reported the DSC thermogram of pure PVA showed the dehydration temperature (Td), the glass transition temperature (Tg) and the melting temperature (Tm) were 30 °C, 114 °C and 222°C respectively. Figure 7 shows a wide peak at a temperature of 150-250 °C. It means that the glass transition process of the film occurs at this temperature, where crosslink modification leads to an increase in the glass transition temperature (Tg) of film. The melting process of the film occurs at a temperature of 243-335 °C (Table 2). The crosslink modification shifts the initial melting temperature (onset melting temperature) to lower and the end-point temperature becomes higher, this shifts due to cross-link stabilize the starch and PVA structure in film [9]. The widening endothermal peak corresponds to the crystallinity of the film. The widened peak indicates the crystallinity of the sample decreases [34]. The uncrosslinked films (P1C1) have a peak at a temperature of 244-267 °C which is possible because of the interaction between the components of arrowroot starch and PVA in the film matrix. This peak does not appear in the cross-linked films.

The enthalpy of melting (ΔHm) indicates the amount of energy required to melt the film matrix. The melting temperature (Tm) is the midpoint of the endothermic peak [34]. Table 2 shows that the greater the amount of citric acid used the value of ΔHm is increasing. This result related to the increase in the amount of the crosslinks formed so that in the melting process it takes more energy to break the bonds formed in the film matrix. This result is consistent with the study of Maiti et al. [35] which reported that the melting point of the starch and PVA film increased due to cross-linking.
The melting process is the beginning of the decomposition of a material. PVA decomposition due to heat are shown in Figure 7. The FTIR spectra of the starch and PVA of thermal change. The temperature shift related to the intermolecular broad peak at 3300 cm$^{-1}$ owned by starch and PVA molecules. The widespread form of the OH group is characteristic of stretching O-H while the band 1148 cm$^{-1}$ is a C-O group. The OH groups owned by starch and PVA molecules. The widespread form of the OH’s peaks evident of the intermolecular interaction between starch and PVA hydrogen bonds [13]. The absorption bands at 935 and 890 cm$^{-1}$ confirm the symmetric stretching of the C-O-C group [36].

The decrease of intensity of peak at 3300 cm$^{-1}$ from 76.14% to 72.45% indicates the decrease of OH group due to the formation of ester bonds by citric acid. The intensity ratio of peaks at 3300 cm$^{-1}$ and 1148 cm$^{-1}$ ($I_{3300}/I_{1148}$) increased in the addition of citric acid from 1.12 to 1.31. It possibly due to the hydrolysis reaction on the glycoside bonds thus increasing the ratio of OH groups to C-O from C-O-C [23].

Table 2. The onset and end-point of melting temperature, melting temperature ($T_m$) and enthalpy of melting ($\Delta H_m$).

| Sample | Onset melting Temperature (°C) | End-point (°C) | $\Delta H_m$ (J/g) | $T_m$ (°C) |
|--------|-------------------------------|---------------|-------------------|------------|
| P1C1   | 269.4                         | 296.0         | 63.19             | 280.9      |
| P1C2   | 252.0                         | 335.8         | 96.37             | 280.5      |
| P1C3   | 250.3                         | 334.9         | 137.78            | 306.9      |
| P1C4   | 246.0                         | 331.1         | 147.05            | 282.9      |

$\Delta H_m$ (enthalpy of melting); $T_m$ (melting temperature)

Figure 7 DSC Thermogram DSC of films Figure 8. TGA analysis of film.
The peak at 1630 cm\(^{-1}\) was obtained in the uncrosslinked film spectra which indicates the presence of a strongly bonded water molecule in the film matrix. These results are consistent with the characteristics of the FTIR spectra of arrowroot starch of the study [36].

**Figure 9.** FTIR spectra of films

3.6. X-ray Diffraction

Diffractogram of uncrosslinked films shows no significant peak which means having an amorphous structure. The arrowroot starch is a native starch with a crystalline form of type A with the crystallinity is 20\% [37]. Heating the arrowroot starch solution in the film preparation formed the gelatinized starch where the starch granules swell and adsorbed the water molecules thus destroying the crystalline structure of starch to form amorphous structure [6].

| Sample name | Relative Cristalinity [%] |
|-------------|--------------------------|
| P1C1        | 0.7                      |
| P1C2        | 0.2                      |
| P1C3        | 1.5                      |
| P1C4        | 6.1                      |

**Table 3.** The relative Cristalinity of films

Figure 10 shows the similarity of XRD patterns of the uncrosslinked and crosslinked films. The uncrosslinked film has a weak peak at 19.5°. While 0.25\% of citric acid concentration (P1C2) appear a peak at 17°. The greater the citric acid concentration than the peak intensity at 17° becomes increased. At a 0.75\% citric acid concentration indicates the presence of two peaks at 17° and 19.5°. According to the results of Faridah et al. [37], arrowroot starch is starch type crystalline A with peaks at 15°, 17°, 20° and 23°. Peaks at 17° and 19.5° indicate the reassociation of linear starch components to form a regular or crystalline structure. The reassociation is possible due to the formation of crosslinks reduce the distance between molecules of starch and PVA so that the greater the chance of forming intermolecular hydrogen bonds.

The crystallinity of the film increases with the addition of citric acid concentration (Table 3). This result is related to the increasing of the intermolecular interaction between arrowroot starch and PVA so that its crystallinity increases. According to Herlina [38], cross-link modification on starch increases the interaction of starch with polyfunctional compounds that can react with the -OH group on the amylose or amylpectin structure which can strengthen the hydrogen bonds in the starch chain.

4. Conclusion

The arrowroot/PVA blend film has been prepared by adding citric acid as a crosslinker agent. PVA used in this research influenced the film properties at the highest concentration. Citric acid greatly affected the properties of the films. The cross-linkings between arrowroot and PVA were developed as ester bonds which are formed from the reaction of hydroxyl groups consisting of starch and PVA with citric acid. The ester bond was confirmed by FTIR spectra. The increase of the amount of citric acid affected significantly on physical, chemical and mechanical properties, water uptake, WVP and crystallinity.
properties. Water barrier level was reduced by decreasing of water uptake and WVP succeeded significantly with increased crosslinking. The elasticity of the films also increases the production of citric acid as a plasticizer in the making of the films as a food packaging material.

Acknowledgment
The authors greatly thank those have supported this research especially to Indonesian Institute of Sciences, The Ministry of Research, Technology and Higher Education of the Republic of Indonesia for funding this research and Synchrotron Light Research Institute – Thailand for providing SAXSIT software for XRD analysis.

References
[1] Ardiansyah Ryan 2011 Pemanfaatan Pati Umbi Garut Untuk Pembuatan Plastik Biodegradable 99
[2] Sarifudin A 2013 Pencirian Bioplastik Komposit Tepung Singkong dan Natrium Alginat dengan Aditif Limonen (Bibliography) a Kulit Jeruk
[3] Hernandez D P, Medina-jaramillo C, Lopez-Cordoba A and Goyanes S 2017 Edible cassava starch films carrying rosemary antioxidant extracts for potential use as active food packaging Food Hydrocoll.63 488–95
[4] Caribé L, Reis B, Oliveira C, Souza D, Betânia J, Cezar A, Larroza I and Izabel J 2014 Food and Bioproducts Processing Active bioocomposites of cassava starch: The effect of yerba mate extract and mango pulp as antioxidant additives on the properties and the stability of a packaged product Food Bioprod. Process.94 382–91
[5] Santacruz S, Rivadeneira C and Castro M 2015 Edible films based on starch and chitosan. Effect of starch source and concentration, plasticizer, surfactant’s hydrophobic tail and mechanical treatment Food Hydrocoll.49 89–94
[6] Wurzburg O. and Szymanski C. 1970 Modified Starches for the Food Industry J. Agric. Food Chem.18 997–1001
[7] Yulianti R and Ginting E 2012 Perbedaan Karakteristik Fisik Edible Film dari Umbi-umbian yang Dibuat dengan Penambahan Plasticizer Balai Penelit. Tanam. Kacang-kacangan dan Umbi-umbian 131–6
[8] Wijayanti A and Harijono H 2014 Pemanfaatan Tepung Garut (Marantha arundinaceae l) sebagai Bahan Pembuatan Edible Paper dengan Penambahan Sorbitol J. Pangan dan Agroindustri3 1367–74
[9] Reddy N and Yang Y 2010 Citric acid cross-linking of starch films Food Chem.118 702–11
[10] Menzel C, Olsson E, Plivelic T S, Andersson R, Johansson C, Kuktaite R, Järnström L and Koch K 2013 Molecular structure of citric acid cross-linked starch films Carbohydr. Polym.96 270–6
[11] Santoso B, Pratama F, Hamzah B and Pambayun R 2015 Karakteristik Fisik dan Kimia Pati Ganyong dan Gadung Termodifikasi Metode Ikatan Silang Agritech35 273–9
[12] Mengatto L, Graciela M, Rubiolo A, Rintoul I and Luna J 2013 Hydrophilic and hydrophobic interactions in cross-linked chitosan membranes Mater. Chem. Phys.139 181–6
[13] Negim E S M, Rakhmetullayeva R K, Zh Y G and Urkimbavea P I 2014 Improving biodegradability of polyvinyl alcohol / starch blend films for packaging applications 3 263–73
[14] Liu B, Xu H, Zhao H, Liu W, Zhao L and Li Y 2017 Preparation and characterization of intelligent starch/PVA films for simultaneous colorimetric indication and antimicrobial activity for food packaging applications Carbohydr. Polym.157 842–9
[15] Pereira V A, de Arruda I N Q and Stefani R 2015 Active chitosan/PVA films with anthocyanins from Brassica oleraceae (Red Cabbage) as Time–Temperature Indicators for application in intelligent food packaging Food Hydrocoll.43 180–8
[16] Liu B, Xu H, Zhao H, Liu W, Zhao L and Li Y 2017 Preparation and characterization of intelligent starch / PVA films for simultaneous colorimetric indication and antimicrobial activity for food packaging applications Carbohydr. Polym.157 842–9
[17] Monjazeb Marvdashti L, Koocheki A and Yavarmanesh M 2017 Alyssum homolocarpum seed
gum-polyvinyl alcohol biodegradable composite film: Physicochemical, mechanical, thermal and barrier properties *Carbohydr. Polym.* **155** 280–93

[18] Râpă M, Grosu E, Andreica M and Hetvary M 2014 Polyvinyl alcohol and starch blends: properties and biodegradation behavior *Journal of Environmental Research and Protection* **11** 34–42

[19] Alcázar-Alay S C and Meireles M A A 2015 Physicochemical properties, modifications and applications of starches from different botanical sources *Food Sci. Technol.* **35** 215–36

[20] Hirsch J B and Kokini J L 2016 Understanding the Mechanism of Cross-Linking Agents (POCl3, STMP, and EPI) Through Swelling Behavior and Pasting Properties of Cross-Linked Waxy Maize Starches *Cereal Chem* **79** 102–7

[21] Luchese C L, Frick J M, Patzer V L, Spada J C and Tessaro J C 2015 Synthesis and characterization of biofilms using native and modified pinho starch *Food Hydrocoll.* **45** 203–10

[22] Setiani W, Sudiarini T and Rahmidar L 2013 Preparasi Dan Karakterisasi Edible Film Dari Poliblend Pati Sukun-Kitosan *Valens* **3** 100–9

[23] Seligra P G, Medina Jaramillo C, Famá L and Goyanes S 2016 Biodegradable and non-retrogradable eco-films based on starch–glycerol with citric acid as crosslinking agent *Carbohydr. Polym.* **138** 66–74

[24] Frost K, Kaminski D, Kirwan G, Lascaris E and Shanks R 2009 Crystallinity and structure of starch using wide angle X-ray scattering *Carbohydr. Polym.* **78** 543–8

[25] Debeaufort F and Voilley A 2015 Lipid-Based Edible Films and Coatings Edible Films and Coating for Food Applications (Springer Science+Business Media) pp 135–210

[26] Darni Y and Utami H 2010 Studi Pembuatan dan Karakteristik Sifat Mekanik dan Hidrofobisitas Bioplastik dari Pati Sorgum *J. Rekayasa Kim. dan Lingkung.* **7** 88–93

[27] Garcia M A, Pinotti A, Martino M N and Zaritzky N E 2009 Characterization of Starch and Composite Edible Films and Coatings Edible Films and Coating for Food Applications pp 169–209

[28] Azahari N A, Othman N and Ismail H 2011 Biodegradation Studies of Polyvinyl Alcohol / Corn Starch Blend Films in Solid and Solution Media **22** 15–31

[29] Sadhu S D, Soni A and Varmani S G 2014 Preparation of Starch-Poly Vinyl Alcohol (PVA) Blend Using Potato and Study of Its Mechanical Properties *Meenakshi Garg* **3** 33–7

[30] Yoon S, Chough S and Park H 2005 Properties of Starch-Based Blend Films Using Citric Acid as Additive . II

[31] Jiugao Y and Ning W 2005 The Effects of Citric Acid on the Properties of Thermoplastic Starch Plasticized by Glycerol 494–504

[32] Pratwi M 2016 *Structural Changes of Arrowroot Starch (Marantha arundinacea L.) as The Impact of Multiple Treatment by Acid Hydrolysis, Debranching, Autoclaving-Cooling, and Heat Moisture Treatment (HMT)*

[33] Hemalatha K ., Parvatikar N and Rukmani K 2015 Influence of ZnO nanoparticles on thermal behavior of Poly Vinyl Alcohol films *Int. J. Sci. Tech. Res.* **5** 106–15

[34] Salleh M S N, Nor N N M, Mohd N and Draman S F S 2017 Water Resistance and Thermal Properties of Polyvinyl Alcohol-Starch Fiber Blend Film *20045*

[35] Maiti S, Ray D and Mitra D 2012 Role of Crosslinker on the Biodegradation Behavior of Starch /Polyvinylalcohol Blend Films 749–59

[36] Valencia G A, Moraes Iz C F, Lourenco R V, Habitante M Q B and Sobral P J do A 2014 *Maranta (Maranta arundinacea L) Starch Properties International Conference on Food properties*

[37] Faridah M S N, Fardiaz D, Andarwulan N and Sunarti T C 2014 Karakteristik Sifat Fisikokimia Pati Garut (Maranta arundinacea) *Agritech* **34** 14–21

[38] Herlina 2010 Karakterisasi Sifat Fisika, Kimia, dan Fungsional Bahan Pati Umbi Gembili (*Dioscorea esculenta L*) Termodifikasi secara Ikatan Silang dengan Natrium Tripolifosfat *Agrotek* **4** 60–7