

THE UTILIZATION OF *BRUGUIRA GYMNOZYSA* MANGROVE FRUIT AS HYDROGEL: THE USE OF PVA/MF/PVP ON THE PHYSICAL-MECHANICAL PROPERTIES OF THE HYDROGEL HEATING METHOD

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Abstract

Bruguiera gymnoryza mangrove fruit (MF) which grows in coastal areas, is one of carbohydrates sources. The flour of MF in the form of starch can be used as a hydrogel that can improve the quality of the product when it mixed with PVA (Polyvinyl alcohol) or PVP (Polyvinyl pirolidone). This research aimed to determine the effect of MF mixture with PVA and PVP on the quality of the hydrogel. MF was obtained from Wonorejo, Surabaya, and East Java. This study used RAL (Completely Randomized Design) with special formulations, the treatments are repeated 3 times, and data analysis using ANOVA, followed by Tukey's test. The results showed that PVA/MF produces a hydrogel product with better water absorption quality, gel fraction, and cross-linking degree than PVP/MF. Meanwhile, a hydrogel with a mixture of PVA/MF/PVP at 1:1 ratio with 2.0% concentration provided the best proportion of water absorption about 292.45%. The FTIR of hydrogel made from MF mixed with PVA and PVP showed absorption at wave number 3645-3600 (narrow) *Nonbonded hydroxy* group - OH stretch. XRD showed that the highest and lowest Crystallinity Index (IC) at 54.75% and 23.10% were identified in PVA/MF and PVA/MF/PVP, respectively. It was concluded that PVA/MF gives the best gel fraction, tensile strength, and hardness. The PVA, PVP, and MF mixture significantly affected water absorption, water content, gel fraction, pH, tensile strength, and hardness. It could improve the hydrogel's physical, mechanical, and structural qualities. Additionally, the average use of PVA/MF had the highest water absorption and gel fraction values. Despite PVA/PVP/MF giving the best results, the quality decreased with the concentration of PVA/PVP used. Finally, the quality of the hydrogel depended on the absorption and gel fraction values.

Keywords: Polyvinyl alcohol, Polyvinyl pirolidone, Tunjung pitat, Mangrove fruit flour.

INTRODUCTION

Bruguiera gymnoryza mangrove is a plant that grows a lot in coastal areas and rich in carbohydrates (Setijawati, 2022). Mangrove fruit (MF) that produces carbohydrates or starch can be used as a hydrogel to increase the use value and benefits (Setijawati et al., 2022). Hydrogel is a polymer that can swell in water or biological fluids while retaining its shape. Despite being hydrophilic due to the presence of -OH, -COOH, -COONH₂, and -SO₃H, it is insoluble in water. Furthermore, the hydrogel can absorb water until it reaches an equilibrium volume with an unchanged, flexible, and elastic shape. The stability and instability in water are the results of the formation of a three-dimensional network structure (cross-linking) in hydrogel (Suliwarno, 2009; Buwalda et al., 2014; Sarmah and Karak, 2022). This polymer can be chemically and physically cross-linked by hydrogen and covalent bond, as well as non-covalent

interactions, respectively. It can be cross-linked by a combination of both through heating.

The hydrogel can be made from synthetic and non-synthetic polymers, carbohydrates, and starch. Polysaccharides in the form of starch have interesting characteristics, including biodegradability, biocompatibility, and bioactivity. The original water-insoluble granules contain two main components, namely (1) 20-30% amylose consisting of a linear chain of α -(1-4-linked-D-glucose) units and (2) amylopectin with a branch chain of α -(1-4-linked-D-glucose) units linked by α -(1-6-linked-D-glucose) bonds, in the proportion of 70–80% (Dragan, 2014; Kenawy, 2014; Ullah, 2015). Original and modified starch were used as raw materials to prepare biodegradable hydrogel. The polymer can be applied in food, medicine, and agriculture. It is used in medical, pharmacy, and biomedical fields (Dragan, 2014; Sarmah and Karak, 2022) for wound dressing (Gopinath, 2022; Wuragil, 2020; Utomo et al., 2016). Furthermore, it can also be applied in agriculture as a soil moisturizer, increasing the slow release of fertilizers with a low negative impact on the environment [Plant] and as an efficient metal ion absorber (Tassanapukdee et al., 2021). The starch content in *Bruguiera gymnorhiza* MF includes amylose 31.6% and amylopectin 26.17% (Jacob et al., 2014). Starch contains abundant hydrophilic (–OH) groups on its surface. Therefore, the content of amylose and amylopectin will determine the characteristics of the resulting film. The ratio of amylose and amylopectin depends on the type of starch, with the amylose content directly proportional to the film's strength (Tanan, 2021).

Preliminary research showed that starch from MF flour yields an easily crackable hydrogel. However, cracking properties can be improved by mixing other materials through cross-linking. The materials that can be used to mix starch in the preparation of hydrogel are polyvinyl alcohol (PVA) and PVP. PVA is a very important polymer widely used in pharmaceutical and biomedical applications (Kenawy, 2014). Meanwhile, PVP is a water-soluble polymer with excellent wetting properties, rapid swelling, excellent film formation, non-toxic and biocompatible, applicable in blood plasma expander polymers, and high storage stability. Its structure can interact with hydrogen bonds, binding insoluble compounds, making them easily soluble. PVP possesses hygroscopic properties, such that it can easily absorb water, form good gels, and has high adhesion. Its swellability can be increased using natural polymers. PVP-based hydrogel formulations can produce preparations that are easy to apply, control, transparent, and flexible. However, both materials have weak mechanical strength properties and lower thermal stability (Ullah, 2015).

The starch which is researched and developed in the preparation of hydrogel, is a material capable of holding large amounts of water, which is one of its essential properties (Sarmah and Karak, 2022). Combining the two polymers or several materials increases the viscosity and produces a flexible, transparent, and soft polymer. Generally, the product is formulated by cross-linking through physical or chemical means using hydrophilic and water-soluble polymers (Husain et al., 2021). Cross-links formation in the preparation of hydrogel can occur physically by heating. Meanwhile, Darwis and Hardiningsih (2010) stated that irradiating a mixture of PVP with starch at various concentrations of gamma rays and irradiation doses of 20 to 40 kGy produce the best results.

Bruguiera gymnoriza MF flour mixed with PVA and PVP can produce hydrogel with better water absorption, tensile strength, gel fraction, and hardness qualities that have not been determined. Therefore, this research aims to test the physical-mechanical properties of hydrogels made from MF flour or MF/PVA/PVP using heating.

MATERIALS AND METHODS

Lindur (*Bruguiera gymnoriza*) MF was obtained from Wonorejo, Surabaya, East Java. It was made into flour (MF), polymer PVP K30 (Polyvinyl pyrrolidone) (China), PVA (Polyvinyl Alcohol) (China), distilled water, plastic wrap, gauze, parchment, and aluminum foil.

Experimental design

The design used was RAL (Completely Randomized Design) with treatments and formulations, as shown in the following Table 1. The treatment is repeated 3 times, and analysis data using ANOVA, followed by Tukey's test were performed on the data using the Minitab 26 program.

Evaluation of hydrogel properties

Water Absorption

Evaluation of hydrogel propertiesThe hydrogel water absorption test follows the modified (Utomo et al., 2016) procedure. The hydrogel was cut into 3 cube-shaped parts with a size of 2 x 2 x 0.5 cm³, dried in an oven at 60oC for 24 hours, and then soaked in distilled water for 24 hours. Furthermore, it was removed from the immersion vessel, the water attached to the wet surface was dried with tissue paper, and the product was weighed (W_b). The hydrogel is dried in an oven at a temperature of 60oC for 24 hours and weighed again (W_k). The following equation (Utomo et al., 2016) is used to calculate the water absorption:

$$\text{Water absorption} = \frac{W_b - W_k}{W_k} \times 100\%$$

W_b = weight of hydrogel after swelling (g)

W_k = dry hydrogel weight (g) in the test

pH

The pH is tested using pH meter by following the procedures of (Martin, 1993; Noviandi, 2016), which is modified by testing the hydrogel material. Firstly, the instrument is calibrated using a buffer solution of pH 4 and 7. The electrodes are rinsed with distilled water and dried. The measurement is performed using 1 g of edible film dissolved in distilled water to 10 ml in a container. Subsequently, the electrode is immersed in the edible film solution and observed until the number indicated by the constant meter matches the pH value of the preparation.

Water Content Test

The water content of the hydrogel was tested according to the method of (Dervish and [5]), which has been modified. The heated hydrogel was cut to size (2 x 2) cm², weighed (W_o), put

into a petri dish, and heated at a temperature of 105°C for 1 hour. Subsequently, it was removed from the oven, cooled, and weighed (W_d). The following equation (Darwis and Hardiningsih, 2010) is used to calculate the water content:

$$\text{Water Content (\%)} = (W_o - W_d) / W_o \times 100\%$$

W_o = initial hydrogel weight

W_t = dry hydrogel weight

Gel Fraction (GF)

The film samples of the size $1 \times 1 \text{ cm}^2$ are dried in an incubator at 37°C for 6 h and then stored in distilled water for 24 h. Similarly, the hydrogel is dried at 37°C for 6 hours. The following formula (Utomo et al., 2016) is used to evaluate the gel fraction (GF) percentage:

$$\text{GF (\%)} = (W_d/W_0) \times 100\%$$

W_o = dry weight of the hydrogel sample

W_d = weight at 37°C after immersion in distilled water

Tensile Strength

The tensile strength was tested according to the procedures of (Fransiska and Reynaldi, 2020) with modifications. The test was performed using the Instron Tester Model made by Toyoseki, Japan, at a speed of 30 mm/minute and temperature of 30°C based on the method stated in ASTM. The hydrogel with this size shape is clamped at both ends with a special device, and the machine is turned ON, hence, the withdrawal process occurs at one of the clamping positions. The magnitude of the breaking stress on the machined hydrogel is measured when the polymer splits in its middle position. The following equation is used to calculate the tensile stress of the hydrogel:

$$\text{Tensile Stress} = F/A$$

F = load from the tool until the material breaks (Kg)

A = cross-sectional area of the material (cm^2)

Hardness

The texture of the material in the form of solid, hard, sticky, and soft is a physical characteristic of food or product. Product with different textures has different response values when subjected to pressure. The hardness test is performed using the TPA (Texture Profile Analyzer) based on pressure on samples with a texture analyzer (TAXT) (Engelen, 2018).

Hydrogel characterization

FTIR functional group

Fourier transform infrared spectroscopy (FTIR) includes the chemical composition of the modified PVA/PVP/CA hydrogel with PVA/MF/PVP material. This is synthesized and analyzed by FTIR (FTIR Spectrum GX System, Perkin-Elmer, USA) using an attenuated reflection mode. The spectrum is obtained in the wave number between 400 and 4000 cm⁻¹ from 64 scans with a resolution of 2 cm⁻¹ (Tassanapukdee et al., 2021).

Crystallinity Index (CI)

The CI test method uses the basic calculation of the area of crystalline and amorphous phases of a material. The X-ray diffractogram obtained is developed using Origin 8.0 software. The following equation (Budi, 2017) is used for calculating the Crystallinity Degree (CD) or CI according to the curve fitting method:

$$CD = A_k / A_t \times 100\%$$

A_k = area of the crystal curve

A_t = total area of the curve (crystal + amorphous)

The measurement of CI is performed twice for each sample using the following formula:

$$\text{Crystallinity Index (\%)} = \frac{\text{Total peak crystalline area}}{\text{Total peak crystalline and amorphous areas}} \times 100$$

SEM (Scanning Electron Microscopy)

SEM is conducted through the cross-sectional morphology of the hydrogel image (JEOL JSM-6510LV, Japan). Before the experiment, the polymer is dried under a vacuum using a lyophilizer. The dried form is then coated with platinum. Finally, the average pore size in each hydrogel group is evaluated using ImageJ software by counting 100 pores from SEM images (Tassanapukde, 2021).

Analysis Data

The experiment is performed in triplicate, and the mean ± standard deviation (SD) is reported. Significant differences between means are calculated using a one-way analysis of variance (ANOVA) at p < 0.05.

RESULTS AND DISCUSSION

The material for *Bruguiera gymnorhiza* MF is from the mangrove tourism area in Surabaya City, East Java, Indonesia, and taken using Google Maps. *Bruguiera gymnorhiza*, called Tunjung Pitat in the local language, has an oval-shaped fruit of mixed where some are reddish yellow and others purplish red or black. Location and *Bruguiera gymnorhiza* fruit are shown in **Figure 1**.

PVA/MF/PVP hydrogel preparation

The heating method prepares the hydrogel following the treatment and formulation in the Table. It starts with weighing the ingredients according to the formulation. Furthermore, each material is mixed with water gradually until dissolved, then individually heated to homogenize the solution. MF flour and water are heated to 85°C. PVA and PVP are dissolved in water and heated to 65°C and 50°C, respectively. Subsequently, the materials are mixed, molded, and placed in a drying oven at 55°C. The hydrogel is removed from the mold after drying and continued with the test. The results of preliminary research on hydrogel preparation from *Bruguiera gymnoryza* MF flour are shown in **Figure 2**.

Evaluation of Hydrogel Properties

Effect of Treatment on the Physical and Mechanical Properties of Hydrogel

ANOVA test showed that each treatment has a significantly different effect ($p < 0.5$) on water absorption, water content, gel fraction, pH, tensile strength, and hardness. The **Table 2** presents the test results.

The water absorption capacity of hydrogel is determined by measuring the swelling equilibrium in distilled water and is expressed in the swelling ratio (S_w). The highest water absorption is obtained in treatment A6, a mixture of PVA/PVP/MF with a 1:1 of PVA and PVP at a concentration of 2%. However, it decreased to a concentration of 2.5%. The PVA + MF provides the highest mean value because they are hydrophilic (Setijawati, 2022b). Due to the high hydrophilic force between PVA, -OH groups can form bonds (Kenawy, 2014). This is because MF is a starch with large hydrophilic properties with a large number of -OH groups and PVA. However, the composition ratio in the PVP/Starch system has a greater degree of development. This system has weak intermolecular H bonds between the C = O and OH groups of PVP and Starch, respectively, while PVP has no intramolecular H bonds. As a result of this situation, water absorption is reduced due to the ability to form a gel fraction. In the PVA/MF/PVP treatment, the MF concentration is greater than that of PVA/PVP. A larger gel fraction is formed due to the increase in PVA/PVP concentration in a ratio of 1:1 at 2.5%. Hydrogel consists of one or more components in a cross-linked system. This is in the form of a three-dimensional network of polymer chains and water molecules that fill the space between cross-linked macromolecules. Finally, the interaction and restraint of water in the system are due to the hydrophilic properties of macromolecules (Sugihartono, 2020).

The water content of a material can be used as an indicator of dryness level and bulk density as well as to determine the weight, texture, and properties of other materials. High-moisture materials tend to have a softer texture, while their dry counterpart tends to have a rougher texture. Hygroscopic materials absorb or release water when left in the open air to achieve equilibrium with the environment (Sugihartono, 2020). The highest and lowest water contents are obtained in treatment A1 (MF) and A7 (PVA/PVP at a ratio of 1:1 with a concentration of 2.5%)/MF, respectively. This is due to MF's high hydrophilicity, which has an -OH group. Amylopectin content higher than amylose in MF results in amorphous properties. This includes the ease of absorbing water, hence, the environment leads to greater water content than PVA

and PVP. Das (2019), stated that starch is a natural substance soluble in water, inexpensive, and very good because of its constitution. Starch exhibits amorphous and crystalline functions despite being composed of alpha-(1,4) glycosidic bonds within amylose and amylopectin polymer structures. The amylose regions of the amylopectin structure and branching points contribute to amorphous and adverse mechanical properties (lower strength and elongation as well as higher brittleness). Theoretically, a hydrogel with low water content has a high absorption capacity, as shown in the **Table 2**.

Gel fraction is a parameter of cross-linking, hence, the gel is not soluble in water. The larger the gel fraction, the smaller the porosity of the matrix and the smaller the ability to bind water. This is in line with other research that the ability of the hydrogel to expand depends on two factors, namely the hydrophilic group and the porosity (Suwarno and Sigit, 2017). The gel fraction's highest and lowest mean value is obtained in treatment A4 (PVA/MF) and A1 (MF), respectively. The material's porosity is thought to be influenced by amylose and amylopectin content. Amylopectin, larger than amylose, makes the material amorphous and porous. MF is amorphous because it has a large degree of hydrophilicity. Furthermore, mixing MF with PVA can increase the crystalline phase of the hydrogel.

Another assumption is that this difference is due to the effect of starch content on the amount of gel fraction (%) produced from the IPN hydrogel (PVP-Starch). The composition ratio in the PVP/Starch system has a greater degree of development. This system has weak intermolecular H bonds between the C = O and OH groups of PVP and Starch. Also, PVP has no intramolecular H bonds. As a result of this condition, water absorption is reduced due to the ability to form a gel fraction.

Table 1: Treatment and formulation in research

Treatment	Formulation (%)			
	PVA	PVP	MF	Distilled Water
A1	-	-	4,5	95,5
A2	2,5	-	-	97,5
A3	-	2,5	-	97,5
A4	2,5	-	4,5	93
A5	-	2,5	4,5	93
A6	2,0	2,0	4,5	91,5
A7	2,5	2,5	4,5	90,5

Description: PVA = Polyvinyl Alcohol, PVP = Polyvinyl Pyrrolidone, MF = Mangrove Flour

Table 2: Effect of Treatment on Physical Mechanical Properties of Hydrogel

Treatment	Water Absorption (%)	Water Content (%)	Gel Fraction (%)	pH	Tensile Strength (N)	Hardness (N/mm ²)
A1	156,47 ± 0,51g	10,35 ± 0,09c	10,23 ± 1,95f	8,3 ± 0,06e	2,08 ± 0,01g	0,01 ± 0,005g
A2	204,53 ± 0,31e	10,34 ± 0,02c	56,27 ± 0,07d	8,5 ± 0,01 bc	31,56 ± 0,46b	1,77±0,1b
A3	187,33 ± 0,41f	10,25 ± 0,04d	36,54 ± 0,05e	8,4 ± 0,1de	21,06 ± 0,01c	1,24 ± 0,030c
A4	243,02 ± 0,36c	10,73 ± 0,01b	73,63 ± 0,08a	8,2 ± 0,05f	40,07 ± 0,02a	2,05 ± 0,020a
A5	245,61 ± 0,17b	10,22 ± 0,02d	60,25 ± 0,22c	8,7 ± 0,06a	16,12 ± 0,08e	1,03 ± 0,010d
A6	292,14 ± 0,28a	11,26 ± 0,02a	65,56 ± 0,12b	8,5 ± 0,06b	8,23 ± 0,09f	0,41 ± 0,001f
A7	233,36 ± 0,09d	10,21 ± 0,07d	60,39 ± 0,15c	8,4 ± 0,06cd	17,13 ± 0,12d	0,89 ± 0,035e

Description: Mean ± stDev. Notations accompanied by the same letter show that they are not significantly different

Table 3: Functional groups with wave number of Hydrogel in various treatments

Reading area	*)	Wave number				
		(MF)**	(PVA)**	(PVA/MF)**	(PVP/MF)**	(PVA/PVP/MF)**
W1	3645-3600 (narrow) Nonbonded hydroxy group, OH stretch 3645-3630 Primary alcohol, OH stretch 3635-3620 Secondary alcohol, OH stretch 3620-3540 Tertiary alcohol, OH stretch 3640-3530 Phenols, OH stretch	3637,95	3614,01	3637,95	3626,34	3619,82
W2	2140-2100 C≡C Terminal alkyne (monosubstituted)					2135,36
W3	1750-1725 Ester 1725-1700 Carboxylic acid	1700,76	1742,12	1742,12	1712,37	1742,12
W4	800-700 Aliphatic chloro compounds, C-Cl stretch 860-800 C-H 1,4-Disubstitution (para) 1310-1290 Vinylidene C-H in-plane bend 1190-1130 Secondary amine, CN stretch	1295,19 ; 794,56	1139,92	1134,12 ; 859,86	1300,99 ; 811,98	

Description: Source:*Nandiyanto et al (2019); ** Author's result

Table 4: Hydrogel CI test results

Sample Code	Total Crystalline Peak	Total Amorphous Peak	Crystallinity Index (%)
A2	1090,33009	2712,60337	40,19
A4	2612,74576	4772,25674	54,75
A5	1420,13911	3954,87293	35,91
A7	805,49296	3486,46676	23,10

Description: A2 =PVA, A4 =PVA/MF, A5 = PVP/MF, A7 =PVA/MF/PVP

The highest and lowest pH is obtained in treatment A5 (PVP/MF) and A4 (PVA/MF), respectively. Therefore, different treatments cause variations in pH. The tensile strength of a material is expressed in the maximum force value produced when the test is performed. The force produced is directly proportional to the tensile strength, which is one essential hydrogel parameter representing its flexibility (Fransiska Dina and Reynaldi, 2020). The highest and lowest mean tensile strength values are obtained in treatment A4 (PVA/MF) and A1 (MF), respectively. PVA/MF has higher tensile strength than MF because the amylopectin content of MF makes the material more amorphous, thereby giving many spaces. PVA fills this space, resulting in the hydrogel being more tightly packed. PVA/MF blending can mask the amorphous properties of MF.

Hydrogel Characterization

Hydrogel functional groups using FTIR

FTIR analysis of PVA/PVP/MF hydrogel samples provides information about the physicochemical changes due to differences in the material mixture treatment. The figure shows the spectrum of this hydrogel. Furthermore, the FTIR results of the PVA-PVP-MF polymer are shown in the **Figure 3** and **Table 3**.

The IR spectrum is divided into three wave number regions, such as far (<400 cm⁻¹), middle (400-4000 cm⁻¹), and near (4000-13000 cm⁻¹). The middle IR spectrum is the most widely used in sample analysis. Furthermore, it is divided into four regions, including 1) single bond (2500-4000 cm⁻¹); 2) triple bond (2000-2500 cm⁻¹), 3) double bond (1500-2000 cm⁻¹), and 4) fingerprint (600-1500 cm⁻¹) (Nandiyanto, 2019).

From **Table 3**, known that W1 is possessed by the treatment of MF, PVA, PVA/MF, PVP/MF, and PVA/MF/PVP at a wave number of 3645-3600 cm⁻¹, non-bonded hydroxy group, -OH stretch. W2 belongs to PVA/MF/PVP. Meanwhile, W3 is owned by MF, PVA, PVA/MF, PVP/MF, and PVA/MF/PVP. W4 is owned by MF, PVA, PVA/MF, PVP/MF, not PVA/MF/PVP. Therefore, all treatments with MF, PVA, PVA/MF, PVP/MF, and PVA/MF/PVP materials have molecule -OH, showing the hydrophilic properties of the hydrogel. The hydrophilicity of the hydrogel is shown through the water absorption test, which has a value between 156.47% to 292.19%. This is in line with (Gyles, 2017), which stated that the hydrophilic properties of the hydrogel are due to the presence of special molecules, such as -OH, -CONH, -CONH₂, and -SO₃H discovered in the gel polymer components, accounting for their different adsorption potentials. Due to its low interfacial stress with water and other biological fluids, the hydrogel swells and expands to become soft and spongy.



Figure 1: (a) (b) Location for sampling *Bruguiera gymnoryza* MF based on Google Maps. Source: Google Map Image, (c) *Bruguiera gymnoryza* fruit (personal documentation)

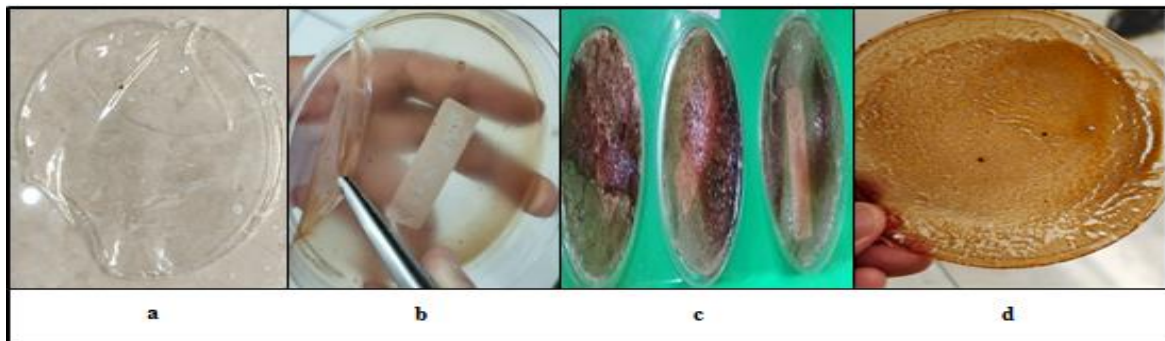


Figure 2: Hydrogel made of (a) PVA, (b) PVA/MF, (c) PVP/MF, (d) PVA/MF/PVP

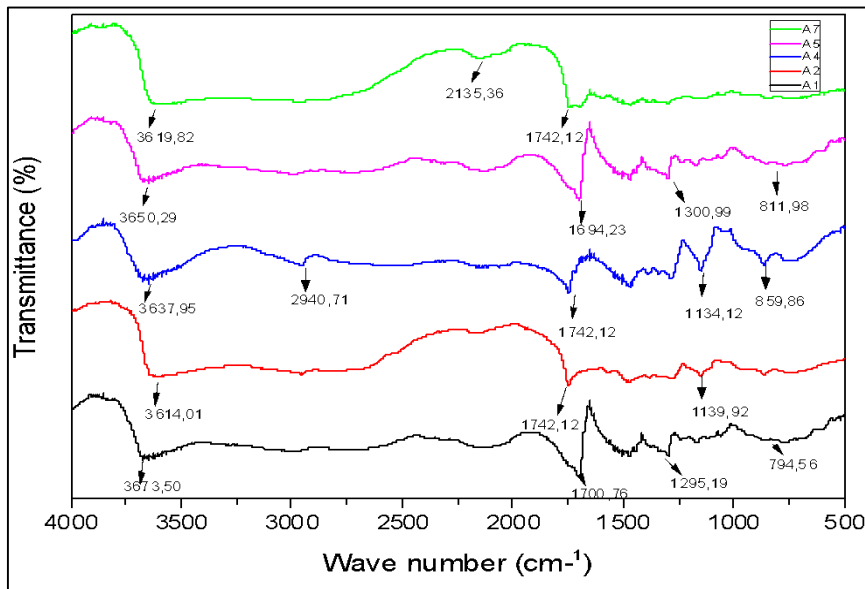


Figure 3: Wave number of hydrogel A1=MF; A2= PVA; A4 = PVA/MF; A5=PVP/MF; A7=PVA/MF/PVP

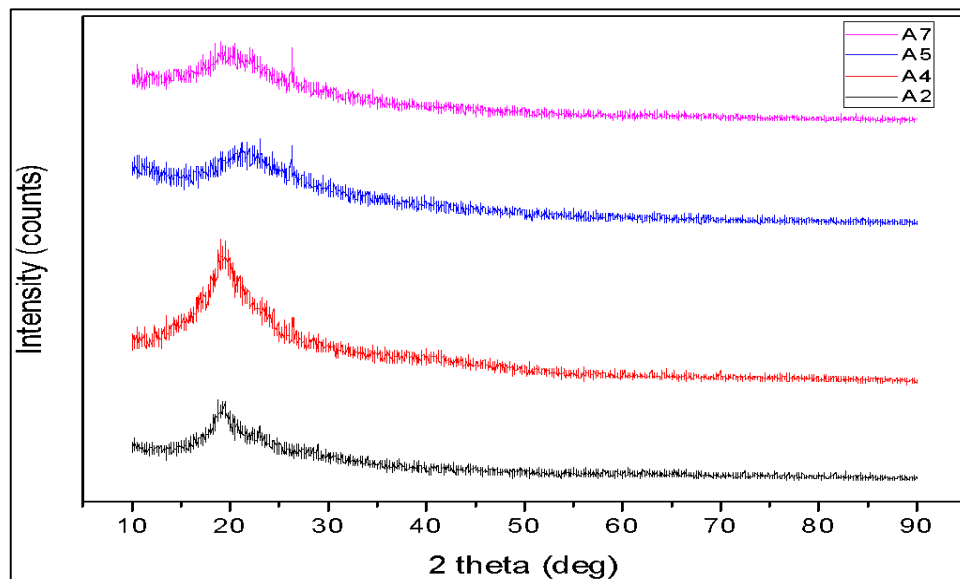


Figure 4: XRD pattern of A2 = PVA; A4 =PVA/MF; A5 =PVP/MF; A7=PVA/MF/PVP

Crystallinity Index (CI) of hydrogel

The pattern in the **Figure 4**. Shows the XRD test results of hydrogel due to different material treatments, and the CI calculation with the basic method of calculating the area of crystalline and amorphous phases obtains the values as shown in **Table 4**.

The CI test results showed that the highest and lowest value is 54.75% and 23.10% in the PVA/MF and PVA/MF/PVP treatments, respectively. The PVA/MF materials mixture has a higher value than PVA in the hydrogel preparation. Meanwhile, the PVA/MF/PVP mixture has the lowest value compared to PVP/MF and PVA/MF. Using the same concentration on MF can affect the interaction between PVA/MF, PVP/MF, and PVA/MF/PVP. Meanwhile, PVP/MF has a lower value than PVA/MF.

This is presumably because the starch in MF contains amylose and amylopectin. The flour has amylose and lipid or fat content of 1.14% (Fadilah et al., 2020). Furthermore, in this research, the amylose and fat contents are 21% and 3.4%, respectively. The presence of amylose-lipid bonds will increase the hardness due to heating. This is supported by (Budi, 2017) which stated that the higher the crystallinity degree of analog rice, the more regular the molecular arrangement of the amylose-lipid complex, hence, the intermolecular forces become stronger. Based on Table, PVA will have an increase in CI when mixed with MF. However, it will decrease CI when the hydrogel consists of PVA/MF/PVP mixture. (Tassanapukdee et al., 2021) stated that there is no active functional group in the PVP structure to form covalent bonds with other polymers. This is because the oxygen atom of the PVP amide group can attach to the Chitosan or CS/PVA network through hydrogen bonds with the available hydroxyl and amino groups. The hydrogen bonding network mechanism to form cross-links occurs through the attachment reaction of the hydroxyl and amine group network. According to the data in Table, PVA, MF, PVP, and their mixtures are in region 1, namely non-bonded hydroxyl stretch at wave

number 3645-3600 cm⁻¹. The amine group is in region 4 with wave number 1190–1130 secondary Amine, CN stretch. In contrast to MF and PVP/MF, PVA and PVA/MF contain an amine group. This is thought to decrease the CI value in PVA/MF/PVP.

SEM (Scanning Electron Microscopy)

The morphology of hydrogel made from MF, PVA, and PVP using SEM is shown in the following **Figure 5**.

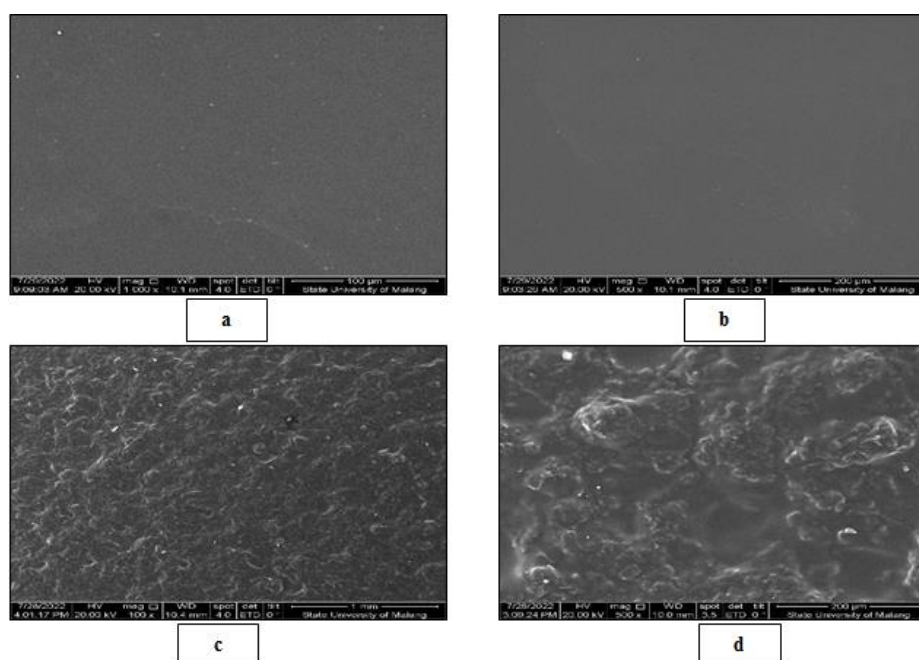


Figure 5: SEM of Hydrogel (a and b) made of PVA/MF at 100X and 500X magnification, (c and d) made from PVA/MF/PVP at 100X and 500X magnification.

CONCLUSION

The PVA, PVP, and MF mixture significantly affect water absorption, water content, gel fraction, pH, tensile strength, and hardness. This can improve the hydrogel's physical, mechanical, and structural qualities. The average use of PVA/MF gives the highest water absorption and gel fraction values. Furthermore, the PVA/PVP/MF mixture gives the best results, but the quality decreases with the concentration of PVA/PVP. The quality of hydrogel depends on the absorption and gel fraction values. Therefore, it is recommended to use PVA/MF or PVA/MF/PVP mixtures to prepare hydrogel to improve the physical-mechanical properties.

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Authors' Contributions

All authors have contributed to the final manuscript. The contribution of each author as follow, Dwi, Yahya, and Tian; collecting data. Dwi and Tian; compiling manuscripts and designing figures. Yahya; critical revision of articles. Dwi; composing the final script.

Conflict of Interest

The authors declare that they have no competing interests.

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Highlight Research

Bruguiera gymnoriza has been analyzed for its utilization as Hydrogel Analysis of the use of a mixture of MF with PVA (Polyvinyl alcohol) and PVP (Polyvinyl pyrrolidone) on the quality of the hydrogel PVA/MF produces a hydrogel product with better water absorption quality, gel fraction, and cross-linking degree.

References

- 1) Bandyopadhyay S, Saha N, Brodnjak UV, and Sáha P. (2019). Bacterial cellulose and guar gum based modified PVP-CMC hydrogel films: Characterized for packaging fresh berries. Food Packag. Shelf Life 22. doi: 10.1016/j.fpsl.2019.100402.
- 2) Budi, F. S., Hariyadi, P., Budijanto, S., & Syah, D. (2017). Kristalinitas dan kekerasan beras analog yang dihasilkan dari proses ekstrusi panas tepung jagung. Jurnal Teknologi dan Industri Pangan, 28(1), 46-54. doi: 10.6066/jtip.2017.28.1.46.
- 3) Buwalda, S. J., Boere, K. W., Dijkstra, P. J., Feijen, J., Vermonden, T., & Hennink, W. E. (2014). Hydrogels in a historical perspective: From simple networks to smart materials. Journal of controlled release, 190, 254-273. doi: 10.1016/j.jconrel.2014.03.052.
- 4) Darwis, D., & Hardiningsih, L. (2010). Potensi hidrogel polivinil pirolidon (PVP)-pati hasil iradiasi gamma sebagai plester penurun demam. Jurnal Ilmiah Aplikasi Isotop dan Radiasi, 6(1), 46-57. doi: 10.17146/jair.2010.6.1.510.
- 5) Das, A., Uppaluri, R., & Das, C. (2019). Feasibility of poly-vinyl alcohol/starch/glycerol/citric acid composite films for wound dressing applications. International journal of biological macromolecules, 131, 998-1007. doi: 10.1016/j.ijbiomac.2019.03.160.
- 6) Dragan, E. S. (2014). Design and applications of interpenetrating polymer network hydrogels. A review. Chemical Engineering Journal, 243, 572-590. doi: 10.1016/j.cej.2014.01.065.
- 7) Engelen, A. (2018). Analisis kekerasan, kadar air, warna dan sifat sensori pada pembuatan keripik daun kelor. Journal Of Agritech Science (JASc), 2(1), 10-15. doi: doi.org/10.30869/jasc.v2i1.173.
- 8) Fadilah, R., Sari, R., & Sukainah, A. (2020). Pengaruh substitusi tepung buah mangrove jenis lindur (*Bruguiera gymnorhiza*) terhadap kualitas mie basah. Jurnal Pendidikan Teknologi Pertanian, 6(1), 65-78.
- 9) Fransiska, D., & Reynaldi, A. (2019). Karakteristik hidrogel dari iota karaginan dan PVA (poly-vinyl alcohol) dengan metode freezing-thawing cycle. Jambura Fish Processing Journal, 1(1), 24-34. doi: 10.37905/jfpj.v1i1.4503.
- 10) GoogleMap. <https://www.google.co.id/maps/place/Wisata+Mangrove+Wonorejo+Surabaya/@7.2994911,112.7830737,24348m/data=!3m1!1e3!4m5!3m4!1s0x2dd7f10aad43d47f:0x3765482949c1cf6d!8m2!3d-7.3087462!4d112.8217729>. Accessed on: 11 November 2022. Time :01.38 p.m. WIB.
- 11) Gopinath, V., Kamath, S. M., Priyadarshini, S., Chik, Z., Alarfaj, A. A., & Hirad, A. H. (2022).

- Multifunctional applications of natural polysaccharide starch and cellulose: An update on recent advances. *Biomedicine & Pharmacotherapy*, 146, 112492. doi: 10.1016/j.biopha.2021.112492.
- 12) Gyles, D. A., Castro, L. D., Silva Jr, J. O. C., & Ribeiro-Costa, R. M. (2017). A review of the designs and prominent biomedical advances of natural and synthetic hydrogel formulations. *European Polymer Journal*, 88, 373-392. doi: 10.1016/j.eurpolymj.2017.01.027.
 - 13) Husain, M. S. B., Al-Ashwal, B. Y., Gupta, A., Sharma, S., Reddy, V. J., Elhag, H. E. E. A., & Soubam, T. (2021). Synthesis of hydrogel films based on PVA, PVP, starch and keratin extracted from chicken feathers wastes for the Potential biomedical applications. doi: 10.20944/preprints202110.0044.v1.
 - 14) Jacob, A. M., Nugraha, R., & Utari, S. P. S. D. (2014). Pembuatan edible film dari pati buah lindur dengan penambahan gliserol dan karaginan. *Jurnal Pengolahan Hasil Perikanan Indonesia*, 17(1), 14-21. doi: 10.17844/jphpi.v17i1.8132.
 - 15) Kenawy, E. R., Kamoun, E. A., Eldin, M. S. M., & El-Meligy, M. A. (2014). Physically crosslinked poly (vinyl alcohol)-hydroxyethyl starch blend hydrogel membranes: Synthesis and characterization for biomedical applications. *Arabian Journal of Chemistry*, 7(3), 372-380. doi: 10.1016/j.arabjc.2013.05.026.
 - 16) Martin A, Swarbrick J, A. Cammarata A. 1993. *Farmasi Fisika*. 3rd Ed., Universitas Indonesia Press, Jakarta.
 - 17) Massie, T., Pandey, E. V., Lohoo, H. J., Mentang, F., Mewengkang, H. W., Onibala, H., & Sanger, G. (2020). Substitusi tepung buah mangrove *Bruguiera gymorrhiza* pada camilan stick. *Media Teknologi Hasil Perikanan*, 8(3), 93-99. doi: 10.35800/mthp.8.3.2020.29434.
 - 18) Nandiyanto, A. B. D., Oktiani, R., & Ragadhita, R. (2019). How to read and interpret FTIR spectroscopy of organic material. *Indonesian Journal of Science and Technology*, 4(1), 97-118. doi: 10.17509/ijost.v4i1.15806.
 - 19) Nofiandi, D., Ningsih, W., & Putri, A. S. L. (2016). Pembuatan dan karakterisasi edible film dari poliblend pati sukun-polivinil alkohol dengan propilenglikol sebagai plasticizer. *Jurnal Katalisator*, 1(2), 1-12. doi: 10.22216/jk.v1i2.1113.
 - 20) Park, S., Baker, J. O., Himmel, M. E., Parilla, P. A., & Johnson, D. K. (2010). Cellulose crystallinity index: measurement techniques and their impact on interpreting cellulase performance. *Biotechnology for biofuels*, 3(1), 1-10.
 - 21) Radoslaw WA. 2003. Radiation-induced crosslinking of cellulose ether with water [Doctoral Dissertation], Gunma University [Japan].
 - 22) Rahayuningdyah, D. W. (2020). Pengembangan formula hidrogel balutan luka menggunakan kombinasi polimer galaktomanan dan PVP. *Pharmaceutical Journal of Indonesia*, 5(2), 117-122. doi: 10.21776/ub.pji.2020.005.02.8.
 - 23) Roy, N., Saha, N., Kitano, T., & Saha, P. (2012). Biodegradation of PVP–CMC hydrogel film: A useful food packaging material. *Carbohydrate polymers*, 89(2), 346-353. doi: 10.1016/j.carbpol.2012.03.008.
 - 24) Sarmah, D., & Karak, N. (2022). Physically cross-linked starch/hydrophobically-associated poly (acrylamide) self-healing mechanically strong hydrogel. *Carbohydrate Polymers*, 289, 119428.
 - 25) Segal, L. G. J. M. A., Creely, J. J., Martin Jr, A. E., & Conrad, C. M. (1959). An empirical method for estimating the degree of crystallinity of native cellulose using the X-ray diffractometer. *Textile research journal*, 29(10), 786-794.
 - 26) Setijawati D. (2022). Structuring the *Bruguiera gymnorhiza* mangrove area for food security in Paciran Village, Paciran District and Labuhan Village, Brondong District, Lamongan Regency, East Java. *EcoEnv & Cons*, 28(3), 1157-1170. doi: <http://doi.org/10.53550/EEC.2022.v28i03.013>.
 - 27) Setijawati, D., Yahya, Y., Kartikaningsih, H., Sukoso, S., Fitri, A. L., & Hidayat, R. I. (2022, April).

- Penggunaan pva/i-caragenan/tepung buah mangrove *Bruguiera gymnorrhiza* terhadap kualitas fisika produk hydrogel. In *Prosiding Seminar Nasional Perikanan dan Kelautan* (Vol. 9, No. 1, pp. 95-102).
- 28) Sugihartono, S., Rahmawati, D., & Priatni, A. (2020). Kemampuan hidrogel komposit berbasis produk samping industri penyamakan kulit dalam menyerap air dan larutan garam. *Majalah Kulit, Karet, dan Plastik*, 36(1), 35-44. doi: 10.20543/mkkp.v36i1.6097.
 - 29) Suliwarno, A. 2009. Sintesis hidrogel karboksimetil selulosa (CMC) dengan teknik iradiasi gamma dan karakterisasinya. *Prosiding Seminar Nasional XVIII Kimia dalam Industri dan Lingkungan. Jaringan Kerjasama Kimia Indonesia, Yogyakarta*, 339-342 [Indonesia].
 - 30) Suwarno, H., & Sigit, R. Kinetika pembentukan fasa hidrida pada zircaloy-4 selama proses gaseous hydriding dengan pendekatan persamaan avrami. *Indonesian Journal of Materials Science*, 18(2), 68-73.
 - 31) Tanan, W., Panichpakdee, J., Suwanakood, P., & Saengsuwan, S. (2021). Biodegradable hydrogels of cassava starch-g-polyacrylic acid/natural rubber/polyvinyl alcohol as environmentally friendly and highly efficient coating material for slow-release urea fertilizers. *Journal of Industrial and Engineering Chemistry*, 101, 237-252. doi: 10.1016/j.jiec.2021.06.008.
 - 32) Tassanapukdee, Y., Prayongpan, P., & Songsrirote, K. (2021). Removal of heavy metal ions from an aqueous solution by CS/PVA/PVP composite hydrogel synthesized using microwaved-assisted irradiation. *Environmental Technology & Innovation*, 24, 101898. doi: 10.1016/j.eti.2021.101898.
 - 33) Terinte, N., Ibbett, R., & Schuster, K. C. (2011). Overview on native cellulose and microcrystalline cellulose I structure studied by X-ray diffraction (WAXD): Comparison between measurement techniques. *Lenzinger Berichte*, 89(1), 118-131.
 - 34) Threepopnatkul, P., Sokjorhor, J., Homchan, P., & Khammee, W. (2022). Preparation of hydrogel with self-healing properties based on poly (vinyl alcohol)/corn starch/zeolite/cellulose nanocrystals for wound dressing applications. *Materials Today: Proceedings*, 52, 2467-2473. doi:10.1016/j.matpr.2021.10.432.
 - 35) Ullah, F., Othman, M. B. H., Javed, F., Ahmad, Z., & Akil, H. M. (2015). Classification, processing and application of hydrogels: A review. *Materials Science and Engineering: C*, 57, 414-433. doi: 10.1016/j.msec.2015.07.053.
 - 36) Utomo, B. S. B., Fransiska, D., & Darmawan, M. (2016). Formulasi hidrogel dari polivinil pirolidon dan k/i-karaginan untuk bahan pembalut luka. *Jurnal Pascapanen dan Bioteknologi Kelautan dan Perikanan*, 11(1), 55-66. doi: 10.15578/jpbkp.v11i1.258.
 - 37) Warkoyo, W., Rahardjo, B., Marseno, D. W., & Karyadi, J. N. W. (2014). Sifat fisik, mekanik dan barrier edible film berbasis pati umbi kimpul (*Xanthosoma sagittifolium*) yang diinkorporasi dengan kalium sorbat. *Agritech*, 34(1), 72-81.