Poly (vinyl alcohol)/glutaraldehyde/Premna oblongifolia merr extract hydrogel for controlled-release and water absorption application

Hendrawan Hendrawan1,*, Fitri Khoerunnisa1, Yaya Sonjaya1, Austina Dwi Putri1

1 Department of Chemistry, Universitas Pendidikan Indonesia, Setiabudi 229, Bandung-40154, West Java, Indonesia
* corresponding author: hendrawan@upi.edu

Abstract. Fertilizer leaching and water slack are the most problems predominantly found in the agriculture practices. Many efforts have been done by promoting a medium for controlling fertilizer release and water retaining in vicinity of plant and soil. In this work, a biodegradable Premna Oblongifolia Merr (POM) extract/polyvinyl alcohol (PVA) composite based hydrogel for controlled-release and water absorption application has been prepared. The hydrogel composite was successfully synthesized through solution mixing of POM and PVA with an aid of crosslinking agent (glutaraldehyde) at optimum composition in volume ratio of 5:5:9, respectively. In particular, the fertilizer (Zinc nitrate) solution was incorporated into hydrogel matrix for controlled release study. The structural morphology of hydrogel composite was investigated by means of Fourier transform infrared (FTIR) spectroscopy and X-ray diffraction. The water absorption capacity and fertilizer-controlled release behaviour of hydrogel composite were evaluated by gravimetric and atomic absorption spectroscopy techniques, respectively. The FTIR spectra showed the evidence of copolymerization of hydrogel precursors, indicated by the shifting of peak intensity and position of several functional groups (O-H, C-H sp³, C=O, C-N, C-O) as a result of interaction between POM extract and PVA moieties which predominantly occurs through intermolecular hydrogen bonding. In particular, the crosslinking of PVA and POM extract mediated by glutaraldehyde was evidenced by the appearance of new peak for –C-O-C moieties owing to the formation of hemiacetal bridges in between polymer backbones. The insertion of fertilizer into hydrogel matrix was sharpen the peaks of hydrogel moieties and led to new peak appearance at 1384 cm⁻¹ (NO moieties), correspond to the interaction with zinc ions. The X-ray diffraction confirmed the modification of structural morphology of hydrogel with fertilizer insertion as indicated by the slight shift of interlayer distance of polymer matrices. The hydrogel composites showed the large water absorption capacity up to 550 % and could retained water in its matrix for almost 3 weeks. Absorption and released studies indicate that the micronutrient interacts chemically with a surface functional group of hydrogel. The released micronutrient should come from the second and the upper layer where it occurs only at high concentration. These results offer the promising applications for the controlled-release and water absorbent materials.

Keywords: hydrogel; Premna Oblongifolia Merr extract; poly (vinyl alcohol); controlled-release; water absorption
1. Introduction

There are at least four major problems in the agriculture practices, i.e. productivity, efficiency, agronomy, and environment, which bind tightly to the fertilizer application and water supplies. Particularly, fertilizer, which is soluble in water, in certain condition, may lead to catastrophic dissolution, generates fast and uncontrollable particles release into its vicinity of plant, giving rise to the excessive fertilizer leaching.

Many efforts have been done to overcome the problems by promoting a medium for controlling fertilizer release and retaining water in the vicinity of plant and soil. Some efforts on slow release fertilizer (SRF) and on controlled release fertilizer (CRF) materials have been reported [1-6]. The CRF has attracted great attention for several last decade due to its compatibility and biodegradability [1, 2], offering great challenges to develop material that more environmentally friendly for agriculture practices.

The CRF hydrogel can be viewed as a three-dimensional framework that can be prepared from synthetic and/or natural polymer. It has significant capability to absorb and to retain a quantity of water, and to maintain the nutrient availability in soils [3, 4]. In general, hydrogel structure consists of hydrophilic group within the polymer framework and can be hydrated in aqueous environment [5]. Shaviv [6] mentioned that network pattern of hydrogel, time release, preparation method are critical factors on hydrogel application as CRF material.

On the other hand, poly (vinyl alcohol)/PVA has been widely used as hydrogel precursor through co-polymerization with other polymer compounds, due to its hydrophilic character. PVA is a synthetic polymer that is soluble in water because of its hydroxyl groups. It is commonly produced by free radical polymerization and subsequent hydrolysis of poly (vinyl acetate) resulting in a fairly wide molecular weight distribution. In environment, PVA is degradable which is depended on the amount of hydroxyl groups [7]. PVA has been commercially produced on a large scale and utilized in various industrial applications such as fibres, films, hydrogels, and glues [8-10].

Our previous work on hydrogel based on natural polymer, (alginate)-PVA-GA (glutaraldehyde), gave a promising characteristic both on physical feature and released behaviour [11]. In this study, we explore a biodiversity i.e. Premna Oblongifolia Merr (POM), a kind of plant species that is easily to be cultivated, abundantly available in the nature, and have biodegradable properties. Besides, the good gel formation of POM is also promising properties that can be applied as precursor on preparation of polymer composites. Furthermore, since, POM predominantly contains –OH groups that contributes to hydrophilic character, it should play important role on water absorption capacity of hydrogel.

Synthesis of hydrogel through co-polymerization of PVA and POM can be facilitated by means of cross-linker agent. Glutaraldehyde (GA) is commonly used as the chemical cross-linker because of its ability to react with functional groups in both protein and carbohydrate, and to provide materials with substantial improvement in tensile properties [12, 13]. Despite glutaraldehyde provides good improvements in mechanical properties, contradictory evidence has been provided on the cytotoxicity of glutaraldehyde-cross-linked materials. However, cytotoxicity of free glutaraldehyde is depended on the concentration used, and up to 8% glutaraldehyde was shown to be non-cytotoxic [14-16]. It has been also reported that glutaraldehyde is one of suitable crosslinker for polymer blending because it has pendant hydroxyl groups [17, 18].

In this study, we attempt to synthesis the CRF hydrogel based on composites of PVA and POM extract with an aid of glutaraldehyde as cross-linker. Specifically, the morphological structure, swelling ratio, water retention, and release behaviour of synthesized CRF hydrogel will be intensively investigated.

2. Experimental

2.1. Materials

*Premna Oblongifolia Merr* (POM), poly (vinyl alcohol) (PVA), glutaraldehyde, methanol, zinc nitrate, sodium hydroxide, and acetic acid. All chemicals are purchased from Merck, Germany.
2.2. Methods
The POM solution was prepared by extracting 2.5 g of dried POM leaves in 250 mL of sodium hydroxide solution at pH 10 for one hour at room temperature (25°C), and then filtrated hereafter. The PVA solution 10% was prepared by diluting 10.0 g of PVA in 100 mL of distilled water, while the glutaraldehyde solution 1.25% was prepared by diluting 1.25 mL of glutaraldehyde in 100 mL of distilled water. The synthesis of hydrogel was carried out through solution copolymerization method by mixing 10.0 mL of PVA 10% and 10.0 mL of POM 1% at 50°C added by 18.0 mL glutaraldehyde 1.25% and homogenizing for 7 minutes, then dried at room temperature. In particular, for released nutrient investigation, 7.5 mL of zinc nitrate solution of 0.25 M was added into hydrogel mixture.

2.3. Characterizations
The crosslinking mechanism of hydrogel and nutrient coated hydrogel were characterized by means of Fourier transform infrared spectroscopy (Nicolet 6700, FTIR; Thermo Scientific, Japan) after pelleting with KBr. The FTIR spectra were investigated with 40 scans at a 2 cm\(^{-1}\) resolution over the range of 1000-4000 cm\(^{-1}\). The surface morphology of hydrogel and nutrient coated-hydrogel were analysed by scanning electron microscopy (SEM) using a model JSM-6330F, JEOL, Japan. Additionally, the X-ray diffraction patterns of hydrogel and nutrient-coated hydrogel were measured at room temperature using the X-ray diffraction (RINT-2300SF, Rigaku, Japan) with MoK\(\alpha\) at 50 kV and 300 mA. Moreover, the water absorbency of hydrogel and nutrient-coated hydrogel were measured by immersing 1 g of the dried hydrogel and nutrient-coated hydrogel into 200 mL of deionized water and allowing to swell at room temperature. After a series of time period, the swollen hydrogel and nutrient coated hydrogel were separated from unabsorbed water by filtering through a 100-mesh sieve aluminium screen for 2 hours. The swollen hydrogel and nutrient coated-hydrogel were weighed and the water absorbency or the swelling ratio of water was calculated using equation (1):

\[
W_A = \frac{(W_s - W_d)}{W_d} \times 100
\]

where \(W_A\) is the water absorbency as the weight ratio of dried hydrogel or nutrient coated hydrogel, \(W_s\) is the weight of the swollen hydrogel or nutrient coated-hydrogel, and \(W_d\) is the weight of the dried hydrogel or nutrient coated-hydrogel [19].

The nutrient released from hydrogel was measured by immersing the nutrient coated-hydrogel into a beaker glass containing 200 mL of deionized water at ambient temperature. After immersion for certain period, the supernatant was taken for analysing the released nutrient amount with an aid of atomic absorption spectroscopy (AA-6200, Shimadzu, Japan). The amount of released nutrient was calculated by equation (2):

\[
\text{the released nutrient} = \left(\frac{\text{nut}_t - \text{nut}_0}{\text{nut}_0}\right) \times 100
\]

where \(\text{nut}_0\) is the initial amount of nutrient in hydrogel and \(\text{nut}_t\) is the amount of released nutrient into the water in time \(t\).

3. Result and Discussion

3.1. Hydrogel formation
The FTIR spectra provide the information of the hydrogel formation from the initiators as well as the crosslinking mechanism. Fig. 1 represents the FTIR spectra of PVA, PVA-GA, and PVA-GA-POM. In general, the similar peaks appear at wavenumber of 3411 cm\(^{-1}\), 2929 cm\(^{-1}\), 1100 cm\(^{-1}\) correspond to the stretching vibration of OH, -CH sp\(^3\) and –C-O-C groups, respectively.
In particular, the FTIR spectrum of PVA indicates the broader peak of around 3400 cm\(^{-1}\) for stretching vibration of \(-\text{OH}\) moieties due to the intra- and extra-molecular hydrogen bonding. Additionally, the peaks at wavenumber of 1720-1737 cm\(^{-1}\), 1440 cm\(^{-1}\), and 1377 cm\(^{-1}\) correspond to stretching vibration of \(-\text{C}=\text{O}\), and bending vibrations of \(-\text{CH}_2\) and \(-\text{CH}_3\) groups, respectively [18-20].

The hydrogel formation through crosslinking can be evidenced by FTIR spectrum, where the interaction of GA and PVA functional groups remarkably modify the peak of \(-\text{OH}\) stretching becomes narrower. This feature indicates the existence of strong interaction between \(-\text{OH}\) of PVA and \(-\text{C}=\text{O}\) of GA to form an acetal-bridge decreasing the content of free \(-\text{OH}\) groups. This result is supported by the evidence of the appearance of peaks at around 2925 and 2854 cm\(^{-1}\) originated from stretching vibrations of \(-\text{C}-\text{O}\)-\text{C} and \(-\text{CH}\) of aldehyde group [18, 21]. Moreover, the peak at 1627 cm\(^{-1}\) corresponds to \(-\text{C}=\text{O}\) should be a sign of the excess of GA [18] and the disappearance of peak at 1400 cm\(^{-1}\) for \(-\text{CH}_2\) and \(-\text{CH}_3\) bending may be addressed to the formation of a more rigid molecules. Furthermore, the addition of POM into PVA-GA induces a slight increase in peak intensity at 1083 cm\(^{-1}\) corresponds to C-O-C stretching vibration and new peaks at 1157 cm\(^{-1}\) and 775 cm\(^{-1}\) indicate the existence of \(-\text{CN}\) and \(-\text{C}-\text{Cl}\) stretching vibrations, respectively, originated from the secondary metabolites of POM. It could be concluded that the synthesized hydrogel contains the functional group of \(-\text{OH}\), \(-\text{CH}^3\), \(-\text{C}-\text{O}-\text{C}\), \(-\text{C}=\text{O}\), \(-\text{CN}\), and \(-\text{C}-\text{Cl}\).

Moreover, the insertion of nutrient into hydrogel matrix significantly increased the peak intensities at around 3350 cm\(^{-1}\), 2929 cm\(^{-1}\) and 1627-1639 cm\(^{-1}\) correspond to \(-\text{OH}/\text{-NH}\), \(-\text{CH}^3\) and \(-\text{C}=\text{O}\) groups, respectively (Fig. 2). It may be inferred that water confined in the hydrogel matrices has been replaced by nutrient molecules. Moreover, the new peak at 1384 cm\(^{-1}\) associates to \(-\text{NO}\) moieties, directly evidences the confinement of nutrient in the hydrogel matrices.
3.2. Structural Morphology of hydrogel

Fig. 3 shows the SEM image of hydrogel at different magnification. Generally, the SEM images indicate a porous material with asymmetrical pore structure and distribution. This porosity should play significant role in water and nutrient absorption.

Fig. 4 demonstrates the XRD patterns of hydrogel and nutrient coated-hydrogel. The XRD pattern of hydrogel shows the sharper peak and less noise than that of nutrient coated-hydrogel, means that the addition of nutrient reduces the crystallinity of hydrogel.
Figure 4. XRD patterns of hydrogel PVA-GA-POM (red) and nutrient coated-hydrogel PVA-GA-POM (blue).

The interlayer distance (d) was calculated using Bragg equation, as in equation (3):

\[ n\lambda = 2d \sin \theta \]  

(3)

while the crystallite size was calculated using Scherrer equation, as in equation (4):

\[ L = \frac{K\lambda}{\beta \cos \theta} \]  

(4)

Where \( \lambda \) is wavelength of X-ray (nm), \( d \) is the distance between atomic lattices, \( \theta \) is angle between the incident and diffracted X-ray, \( L \) is crystallite size parameter, \( K \) is Scherrer factor, \( \beta \) is line broadening at half the maximum intensity (FWHM) (in rad). As shown in the Table 1, the crystallite size of hydrogel is higher than that of nutrient coated-hydrogel. This means that hydrogel is more ordered than nutrient coated-hydrogel. The addition of nutrient into hydrogel matrices is supposedly modified the interlayer distance become less order/irregular and consequently decreases its crystallite size.

| Peak | Hydrogel | Nutrient coated-hydrogel |
|------|----------|--------------------------|
|      | Position (2θ) | d (nm) | L (nm) | Position (2θ) | d (nm) | L (nm) |
| 1    | 9.65     | 0.423  | 4      | 9.80       | 0.416  | 12     |
| 2    | 12.26    | 0.333  | 17     | 12.36      | 0.330  | 12     |
| 3    | 22.64    | 0.181  | 23     | 22.71      | 0.180  | 12     |
| 4    | 26.76    | 0.154  | 15     | 26.88      | 0.153  | 10     |
| 5    | 29.99    | 0.137  | 19     | 30.04      | 0.137  | 10     |
3.3. Swelling ratio of hydrogel and nutrient coated-hydrogel

Fig. 5 shows the swelling ratio of hydrogel and nutrient coated-hydrogel. The water absorption amount in hydrogel and nutrient coated hydrogel remarkably increases in the time interval less than 2 days and it remains constant after 2 days’ observation, indicating the absorption equilibrium has been reached. In particular, hydrogel has larger water absorption capacity (550%) that of nutrient coated hydrogel (140%). This result suggests that nutrient could reduce vacancies in three-dimensional framework of hydrogel to absorb water molecules and/or could block the surface moieties of hydrogel to interact with water molecules. Consequently, the ability of hydrogel to accommodate water molecules notably decrease.

![Figure 5. Swelling ratio of hydrogel (red) and nutrient coated-hydrogel (blue).](image)

3.4. Water Retention of hydrogel and nutrient coated-hydrogel

Fig. 6 demonstrates water retention of hydrogel and nutrient coated-hydrogel. Similar to water absorbency, hydrogel has larger water retention (4.8%) than that of nutrient coated-hydrogel (1.4%) within observation period up to 3 weeks. Interestingly, within a week, the tendency of water retention of hydrogel and nutrient coated hydrogel are alike, where, the notable amount (up to 60%) of water is released from hydrogel matrices. However, after a week, the amount of released water is not as high as the previous one. Based on the observation result, the hydrogel and nutrient coated-hydrogel can retain water up to almost 3 weeks. The difference amount of released water from hydrogel and nutrient coated-hydrogel can be explained as follow: the strong interaction of water molecules with hydrogel moieties through inter-molecular hydrogen bonding leads to increase water retention in hydrogel matrices. Since the coated nutrient gave the possibility to block either surface moieties or cavity of hydrogel, thus weakening the interaction between hydrogel and water molecules, consequently, water molecules is easier to be released.
3.5. Nutrient released behaviour

The zinc nitrate solution was employed as nutrient matrix on hydrogel. In this study, the concentration of zinc nitrate solution was varied (0.196 ppm; 0.410 ppm; 0.798 ppm; 0.903 ppm; 1.077 ppm). A small dimension of hydrogel (1 cm x 1 cm x 0.3 cm) was immersed into nutrient solutions for exactly 18 minutes, and released Zn in the solution was considered as the absorbed nutrient by hydrogel. The nutrient coated hydrogels are then immersed in distilled water for approximately 18 minutes. The released nutrient was determined by measuring the concentration of Zn in the distilled water by means of AAS equipment.

Fig. 7 shows that the release occurred only at high nutrient concentration, even though at maximum absorption the release clearly did not occurred. It could be suggested that at the concentration smaller than 0.8 ppm, the interaction between nutrient and hydrogel matrix is quite strong. At higher concentration, the nutrients are not stacked directly onto hydrogel matrix but it is distributed as the second layer with a weaker interaction. The higher the layer level, the weaker the force governs the nutrient. At the first layer, the interaction between nutrient and the hydrogel matrix should be in the order of chemical interaction, whereas for the second and the higher layers the interaction should be in the order of physical interaction. On the other hand, in water, zinc may form a charged complex so that it can be bonded tightly on –OH functional group at the surfaces of pores in hydrogel matrix.
4. Conclusion
We have successfully synthesized hydrogel PVA-GA-POM which is promising to be applied for green agricultural practices. The crosslinking of PVA and POM extract mediated by glutaraldehyde was evidenced by the appearance of new peak for –C=O-C moieties owing to the formation of hemiacetal bridges in between polymer backbones. The insertion of fertilizer into hydrogel matrix was sharpen the peaks of hydrogel moieties and led to new peak appearance at 1384 cm$^{-1}$ (NO moieties), which correspond to the interaction with zinc ions. The X-ray diffraction confirmed the modification of structural morphology of hydrogel with fertilizer insertion. The hydrogel composites showed the large water absorption capacity up to 550 % and could retained water and fertilizer in its matrix for almost 3 weeks with the remained content was about 10%. Absorption and release study indicated that nutrient interact chemically with a functional group at the surface in hydrogel cavity. The released nutrient should be formed the second and higher layer as it occurred only at high concentration condition. This result offers the promising applications for the controlled-release and water absorbent materials.

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