Materials Physics and Mechanics 42 (2019) 141-150 Received: December 25, 2018

PREPARATION AND PHYSICO-CHEMICAL PROPERTIES OF GRACILARIA/PVA/GA/CNT-BASED HYDROGEL FOR SLOW/CONTROLLED RELEASE MATERIAL

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Abstract. In this study, we synthesized a hydrogel from the extract of *gracillaria* (GR), poly-(vinyl alcohol) (PVA), glutaraldehyde (GA), and carbon nanotube (CNT). To confirm the synthesis of hydrogel, several characterizations were done, including fourier transform infra red (FTIR) and scanning electron microscope (SEM). Analysis on the material performance under various parameters (such as swelling ratio and release behavior of potassium from hydrogel into aqueous media) was also carefully evaluated based on weight measurement and flame-photometry instrumentation. FTIR spectra showed that the interaction of hydrogel components (GR, PVA, GA, CNT and Kalium-related material) involved some functional groups such as C-O, C-N, C=O, C-H sp^3 as well as O-H which predominantly occurred through hydrogen bonding. The swelling ratio of technical-grade PVA-based hydrogel was higher than that of pro-analytical-grade. The hydrogel showed a typical slow release behavior for potassium ion with the release rate is 8.89 ppm for first ten minutes and the release rate average is 0.0134 ppm/minutes for the normal phase.

Keywords: hydrogel, *gracilari*a, poly-(vynil alcohol), CNT

1. Introduction

Due to its potentiality in wide range of application, especially for slow/controlled release components that are available in fertilizer, drug delivery, ion exchanger, and absorbent materials, hydrogel has been becoming an attractive material and being a great interest of many scientists [1,2]. The use of hydrogel as a medium for a slow/controlled release fertilizer is now getting popular, indicating that there is a positive trend on lifting up the possible applications in practical agriculture. Moreover, exploration of new possible resources for preparing hydrogel matrixes has evidently become a hot topic within two past decades.

Among the main sources in developing a hydrogel for slow/control-release fertilizer holder, poly-(vinyl alcohol) (PVA) and gluteraldehyde (GA) are two main materials frequently used [3]. PVA is a synthetic polymer that is water soluble because of its hydroxyl groups. PVA has a relatively simple chemical structure with a pendant hydroxyl group. PVA is also a non-toxic synthetic polymer and has been available in large scale commercial production. This material is also utilized in various industrial applications, such as fibers, films, hydrogels, and glues [4,5].

For searching environmental compatibility, many scientists have been concerned on incorporating natural polymers into hydrogel matrix. Among many possible sources for natural polymer, red alga has become a major concern because of its alginate content. Alginate is an anionic linear polysaccharide composed of two saccharides. Alginate can be regarded as a binary copolymer composed of α-I-guluronic acid (G) and β-D-mannuronic (M)

http://dx.doi.org/10.18720/MPM.4212019_12

that are covalently bonded through 1,4-glycosidic linkage and arranged into either homopolymeric block (MM and GG) or alternating block (MGMG) along the polymeric backbone [4-12].

Accordingly, the polymer blend (PVA with alginate) can generate the polymeric materials, improving physical properties, lowering cost of basic polymer materials, simplifying the process ability in the film formation, and making the material biologically acceptable [3,10]. Both polymers are hydrophilic, making combination of PVA and alginate to bring positive impacts on improving chemical, physical, and mechanical properties [11,12].

Other potential material that could be used to modified the properties of hydrogel- based controlled-release fertilizer is carbon nanotube (CNT). Carbon nanotubes are nano-scale carbon materials having unique mechanical and thermal properties, offering many advantages for application in various fields. In addition to the distinctive characteristics of CNT (i.e., superior surface area, high electrical conductivity, and low percolation properties when it is dispersed into polymer matrix), CNT has been selected as one of the excellent candidates of polymer filler [13]. The insertion of CNT into polymer matrix can improve physico-chemical properties of polymer [14].

Potassium, in its various forms, plays somewhat important roles in plant growth system. Comprehension of its release behavior into its vicinity may give many valuable insights in developing potassium-based fertilizer system. Release and sorption behavior of a chemical substance from a hydrogel into its vicinity and permeation of a chemical from one phase to another separated by a membrane are affected by several physical and chemical conditions of its environment. It was found that desorption of kalium from PVA-Borate hydrogel was favorable in the aqueous system. The polarity of solvent influences the kinetics of desorption [15]. In other works, it was concluded that the release behavior of a composite lignin-based hydrogel, called LBPAA, is sensitive to pH, temperature, and ionic strength [16].

In this study, *glacilaria sp* and CNT were incorporated into PVA/gluteraldehyde polymer matrix, and its performance such as swelling power and its release behavior were examined. The study used potassium chloride as the working material release.

2. Material and method

2.1. Material

Several materials were used: *Gracillaria sp* (taken from regional farmer), poly-(vinyl alcohol) pro analytical-grade (*Mr* 6000) (Merck, Germany), poly-(vinyl alcohol) technical-grade (Brataco, Indonesia), glutaraldehyde (25% pro analytical-grade; Merck, Germany), methanol (96% pro analytical-grade; Merck, Germany), sulphuric acid (97%; pro analytical-grade; Merck, Germany), acetic acid (pro analytical-grade; Merck, Germany), graphene oxide (Japan), multiwall carbon nanotubes functionalized (Japan), and potassium chloride (KCl; pro analytical-grade; Merck, Germany).

2.2. Method

Preparation of Reactants. PVA solution was prepared by dissolving 20 mg of PVA in 100 mL of deionized water, and stirred while heated at 90°C for about 3 hours. Crosslinker solution was prepared by mixing methanol (50%), acetic acid (10%), sulfuric acid (10%), and glutaraldehyde (1,25%) with a volume ratio 3:2:1:1, respectively. CNT dispersion was prepared by dissolving 1 mg of CNT into 100 mL of graphen oxide solution (1% w/v in deionized water). Then, the solution was sonicated for about 30 minutes. *Gracillaria sp* extract was prepared by macerating 40 g of dry-powdered *gracillaria* (100 mesh) in 200 mL of methanol solution (70%) for about 96 hours, and after while the macerated solution was separated from the residue.

Preparation of hydrogel. The GR/PVA/GA/CNT hydrogel was prepared by mixing the extract of *gracillaria*, PVA solution, crosslinker solution, and CNT solution with a volume ratio of 2:2:2:1, respectively. The technique was as follow: a quantity of PVA solution, crosslinker solution, and CNT solution were successively poured into a quantity of extract of *gracillaria sp*, then stirred gently using magnetic stirrer at 50°C until it is homogenous. The homogenized solution was poured into a hydrogel mold (bar coating plate) and dried in an open air for about five days. The GR/PVA/GA hydrogel was prepared in the same method but it was prepared using a volume ratio of 1:1:1 for GR, PVA, and GA, respectively.

Swelling Ratio. Swelling ratio parameter of the hydrogel was determined by soaking a quantity of dried hydrogel (the mass is exactly known as W_0) into 25 mL of deionized water and allowed to swell at room temperature. After 10 minutes, the swollen hydrogel was separated from the rest of deionized water and drained by filtering using a 100-mesh of aluminum sieve, weighed, and noted as W_t. The swelling ratio of water (SR) was calculated using equation (1).

$$SR = \frac{(W_t - W_0)}{W_0} \times 100, \tag{1}$$

where W_0 is the weight of dried hydrogel, and W_t is the weight of the swollen hydrogel [17].

Release behavior examination. As much as 4 pieces of the GR/PVA/GA/CNT hydrogel with a specific dimension (1 cm × 1 cm × 0.04 cm) was soaked into 200 mL of KCl 1.00 M solution for about 48 hours. Then, after they were dried for about 30 minutes, the 4 pieces of mounted hydrogel is named as GR/PVA/GA/CNT-K. The rest of potassium ion in the solution was determined using the flame-photometer. To examine the desorption profile, the GR/PVA/GA/CNT-K was immersed into 200 mL of deionized water in a beaker glass and continuously stirred. In the certain time, 10 mL of the solution was taken. Then, 10 mL of deionized water was added to the rest of solution to maintain the total volume to be constant. The potassium content in the sampled solution was then determined using a flame-photometer.

2.3. Characterizations

During this study we used a Fourier Transform Infra Red (FTIR; Shimadzu, Japan), Scanning Electron Spectroscope (SEM; JEOL JSM-6510LA, JEOL, Japan), Flame-photometer Corning 410 (CIBA-Corning, Madrid, Spain).

3. Results and Discussion

3.1. Material structure and morphology

The typical FTIR spectrum for GR/PVA/GA, GR/PVA/GA/CNT, and GR/PVA/GA/CNT-K were represented in Fig. 1. It could be noticed in Fig. 1 that the three spectra of hydrogel demonstrated the peaks at the same wavenumber, but they have different intensities, which means that the GR/PVA/GA hydrogel becomes the main part in all modified hydrogel. The addition of CNT and/or CNT-K into the GR/PVA/GA hydrogel did not generate any structural changes. It is most likely that CNT and/or CNT-K stick physically onto hydrogel framework.

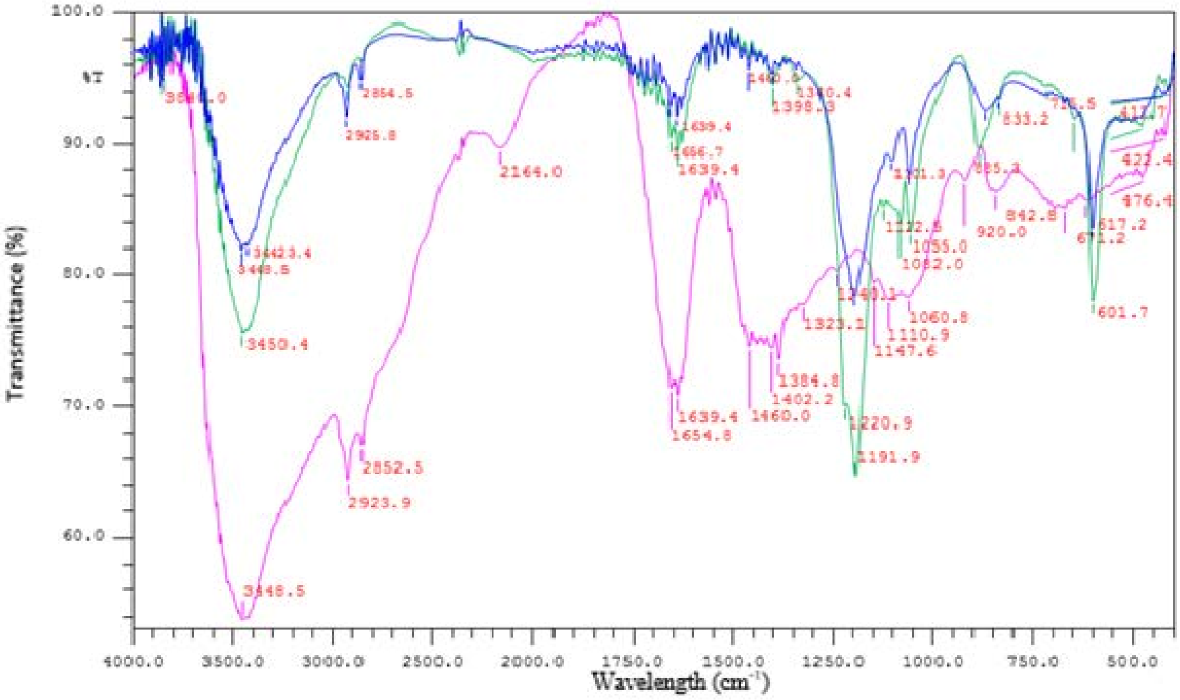

Fig. 1. FTIR spectra of GR/PVA/GA (blue line), GR/PVA/GA/CNT (green line), and GR/PVA/GA/CNT-K (purple line)

The FTIR spectra of GR/PVA/GA, GR/PVA/GA/CNT, and GR/PVA/GA/CNT-K have the absorption peaks at wavenumbers of 3400 cm^{-1} for O-H, 2800-2900 cm^{-1} for C-H stretching from C-H sp^{3}, 1600 cm^{-1} for C=O specific from aldehyde [18], 1200 cm^{-1} for C-N, and 1100 cm^{-1} for C-O/C-O-C. There was a shifting of peak for OH at GR/PVA/GA/CNT, where the peaks for O-H at GR/PVA/GA/CNT is wider than that of GR/PVA/GA, supposedly caused by existence of intramolecular and intermolecular interaction (hydrogen bond) between O-H and CNT. Addition of CNT and/or CNT-K into GR/PVA/GA/CNT framework strengthen the intensity at the adsorption peaks of 3400 cm^{-1}, 2900 cm^{-1}, 1600 cm^{-1}, and 1100 cm^{-1}, for O-H, C-H aldehyde, C=O, and C-O functional groups, respectively. This peaks are different from the types of carbon material [19].

Surface morphologes of GR/PVA/GA, GR/PVA/GA/CNT, and GR/PVA/GA/CNT-K were determined using the SEM as shown in Fig. 2. The images were taken at the cross sectional position with the angle 80 degrees. The SEM images in Fig. 2 show that the surfaces of GR/PVA/GA, GR/PVA/GA/CNT, and GR/PVA/GA/CNT-K are not smooth, but rather rough, for which the tension on the surfaces could provide active sites for adsorbing any charged particles. It is look likely that the level of surface roughness increased in the series of GR/PVA/GA, GR/PVA/GA/CNT, and GR/PVA/GA/CNT-K hydrogel.

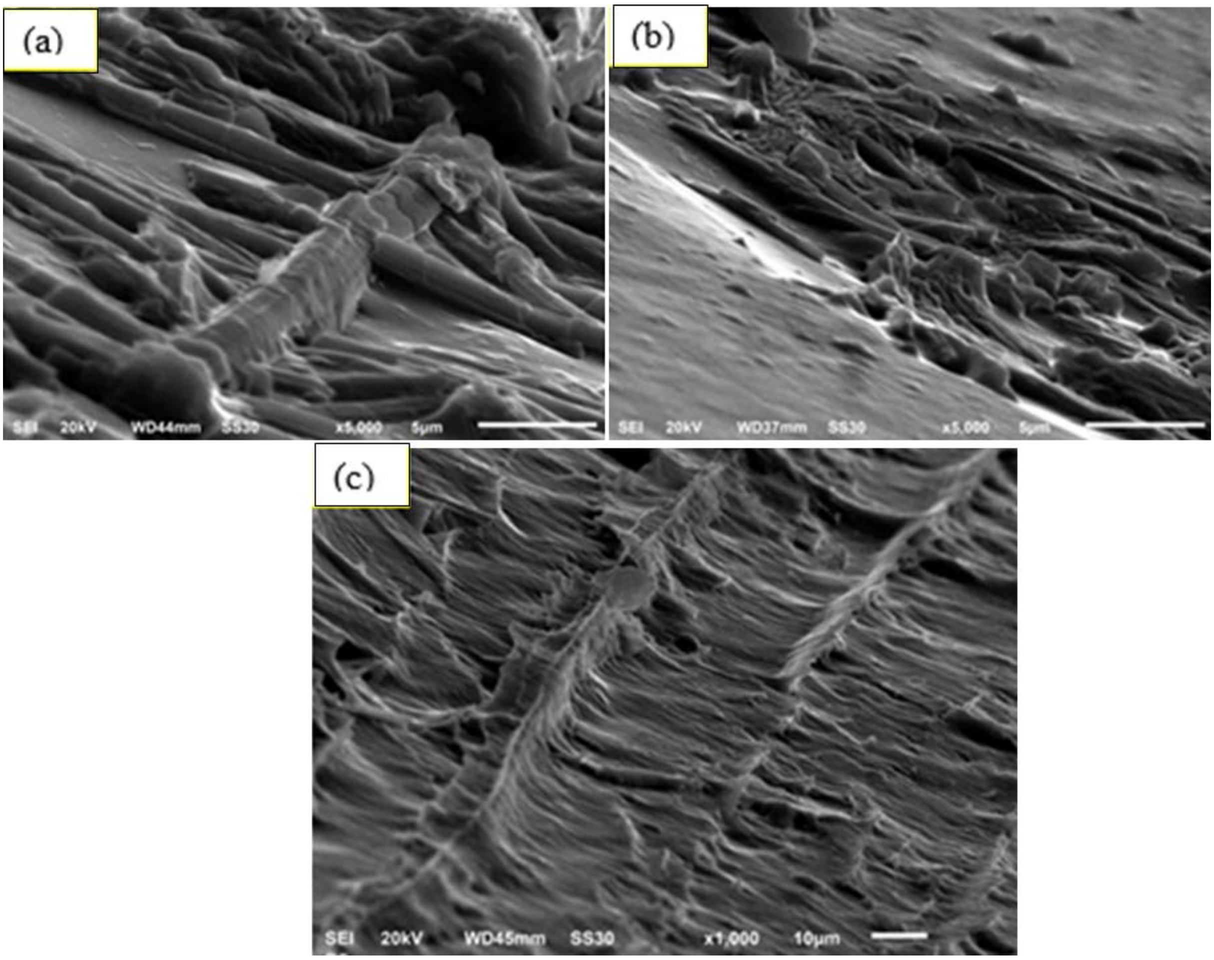

Fig. 2. SEM images of hydrogel: (a) GR/PVA/GA (5000 times), (b) GR/PVA/GA/CNT (5000 times), and (c) GR/PVA/GA/CNT-K (1000 times)

3.2. Material performances

In this work, the performance study of hydrogel was focused on swelling ratio and release behavior parameters.

Swelling Ratio. The typical feature of swelling ratio of GR/PVA/GA/CNT hydrogel based on the variation of PVA purity-grade were represented in Fig. 3. In this case, the GR/PVA/GA/CNT hydrogel where the PVA is in technical-grade is marked as GR/PVA/GA/CNT (TG), while the GR/PVA/GA/CNT hydrogel where the PVA is in pro analytical-grade is encoded as GR/PVA/GA/CNT (PAG).

Fig. 3 represents the plot of swelling ratio versus immersion time of GR/PVA/GA/CNT hydrogel prepared using PVA with technical and pro analytical grades. The hydrogel prepared using PVA technical-grade has a higher swelling ratio compared to that of hydrogel prepared using PVA pro analytical-grade. Utilization PVA technical-grade produced hydrogel with a high capacity in swelling ratio parameter, which may be caused by its high flexibility in absorbing water. The viscosity of PVA in technical-grade is lower than that in pro analytical-grade, in which this is because the intermolecular interaction is easier to form [20].

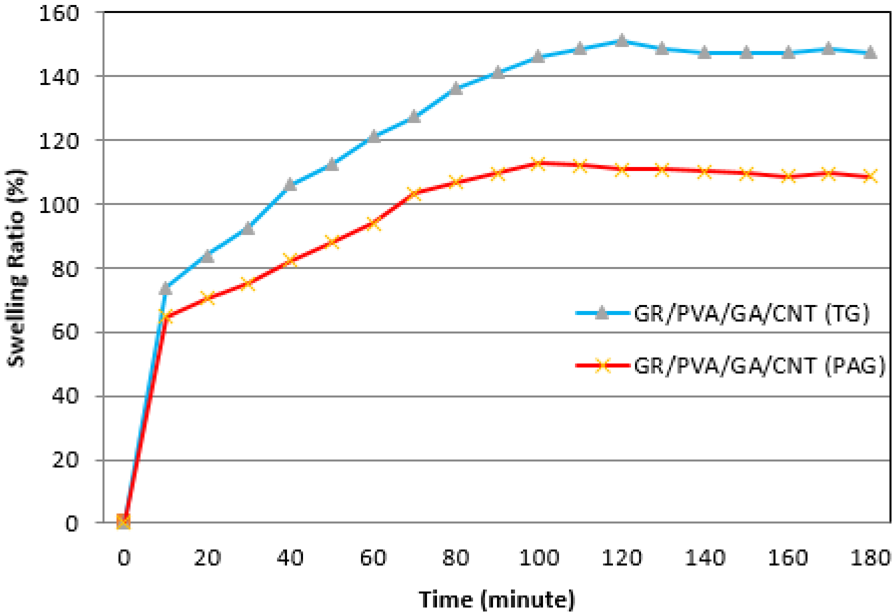

Fig. 3. Swelling Ratio of various GR/PVA/GA/CNT hydrogel as function of time of immersion

Furthermore, effect of addition of potassium ion on swelling ratio of GR/PVA/GA/CNT hydrogel is presented in Fig. 4. The addition of potassium ion into the GR/PVA/GA/CNT hydrogel matrix increases the swelling ratio of the hydrogel both for hydrogel prepared using PVA technical and pro analytical-grades. The graphical profile on the Fig. 4 shows that the presence of potassium ions increases the hydrogel accommodation capacity of water. Although the exact mechanism could not be determined yet, the ability of potassium ions to capture water seemingly plays an important role in achieving the conditions of increasing the hydrogel absorption capacity. The increases in the hydrogels flexibility are due to the presence of potassium ions. They can be inferred from the graph of swelling profiles of GR/PVA/GA/CNT-K (TG) and GR/PVA/GA/CNT-K (PAG) versus time, indicating that the hydrogels are still be able to make flexing at the time of immersion in long period (about 8 days).

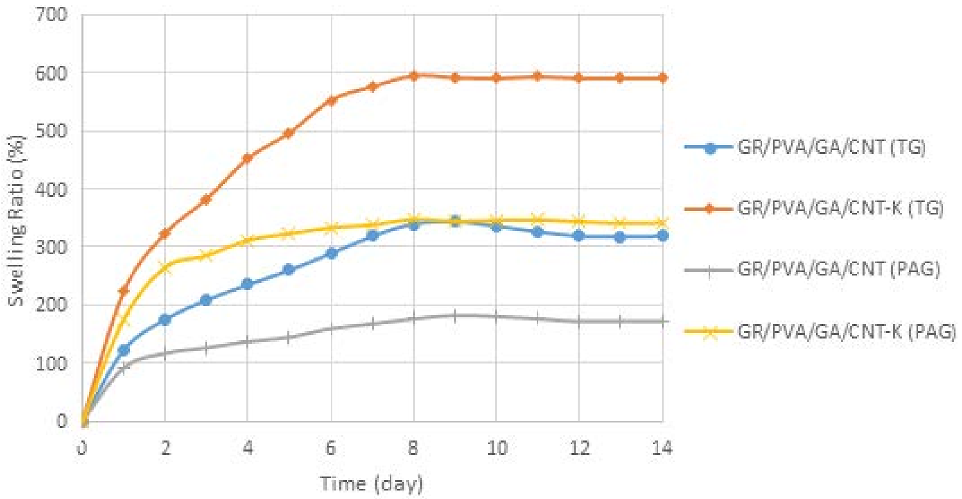

Fig. 4. Profile of Swelling Ratio (SR) of GR/PVA/GA/CNT hydrogel with and without potassium ion [Note: (TG = use technical-grade PVA, PAG = use pro analytical-grade PVA)]

Potassium Release Behavior. The potassium release profile from the loaded hydrogel as a function of time is given in Fig. 5. The release behavior pattern potassium from hydrogel matrix into aqueous phase, as demonstrated in Fig. 5, shows that the overall time release could be divided into three time periods, i.e., the initial period (first five minutes), followed by transient period (between 5 and 10 minutes), and normal period. These periods were attained after 10 minutes of the desorption processes. The pattern of the releasing profile is quite similar to result found by other researcher for potassium chloride release [21,22]. The graph in the Fig. 5 shows that at the initial period, there was a sudden dissolution of potassium chloride into bulk. This fact could be inferred that at the initial period the potassium release was mainly occurred from the surfaces of hydrogel into bulk, which was most probably followed by the occurrence of solvent intrusion into the hydrogel. At the transient period, the release seemed to be the combination between surface release and the release of potassium from the inner part of gel into solvent, where the rate of inner desorption gradually increased as the surface release decreased. At the normal period, the releasing phenomenon may be expected only or mainly from the inner part of gel into solvent. The excessive potassium releases in the early period. Typically, the time period was from zero to five minutes, indicating that most of potassium chloride did not exhibit the inner part of the gel but adsorbed at the surfaces. This condition provoked the occurrence of catastrophic dissolution when the loaded hydrogel was immersed into solvent. Furthermore, if we take the 10th minute of the initial time in the normal releasing phenomenon and the 80th minutes (as the longest limit of observation time), the average of release rate in the time period is 0.0134 ppm per minute.

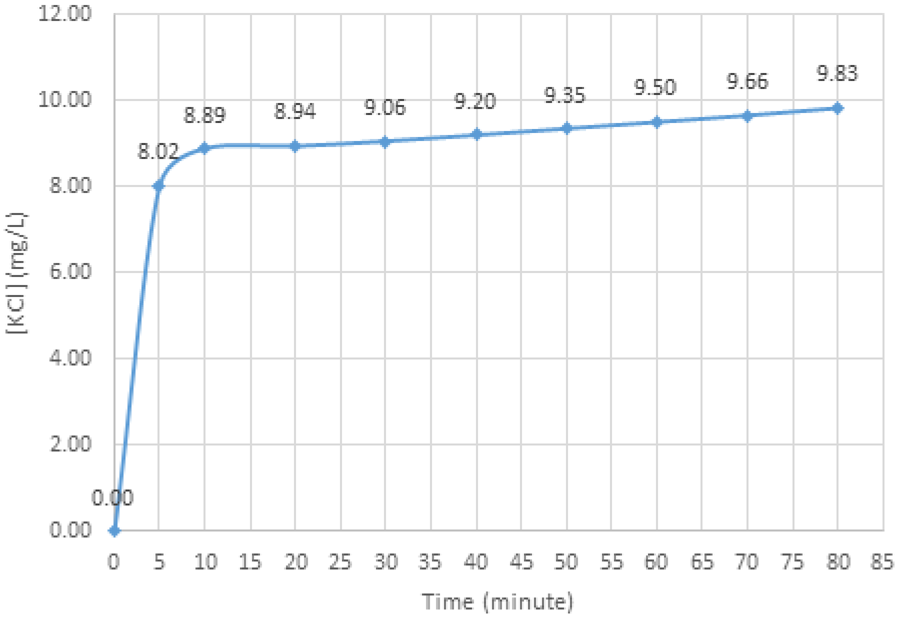

Fig. 5. The total desorbed potassium chloride into aqueous phase during the dissolution processes

It is interesting to look deeper on the release phenomenon after 10 minutes of the processes. The graph on the Fig. 5 demonstrates that there was an increase in the quantity of potassium released over the same time period. The increase in the release rate seems to be fairly regular. The increment of the releasing rate may be visualized in term of the value differences between the concentrations of KCl in the series of releasing time. The typical feature of the graph is presented as Fig. 6. With increasing time, there should be a decrease in the concentration inside the gel. If the process was done within a period of 10 to 80 minutes, the amount of potassium released is very small compared to the initial concentration. Thus, the concentration inside the gel can be practically unchanged. At the period between 10 and 40 minutes, the increase in release rate can be expected as a result of broadening the pores within the hydrogel, allowing material run less retarded from the hydrogel into the environment. The stagnant release rate, between 40 and 70 minutes, can be explained as the maximum expansion of gel volume, which was attained at the 40th minute of the gel immersion. Meanwhile, the sudden change in release rate after 70th minute of immersion could be due to physical deformation such as gel abrasion or torn. This assumption is also supported by the fact that the swelling ratio of hydrogel increases with the length of immersion time.

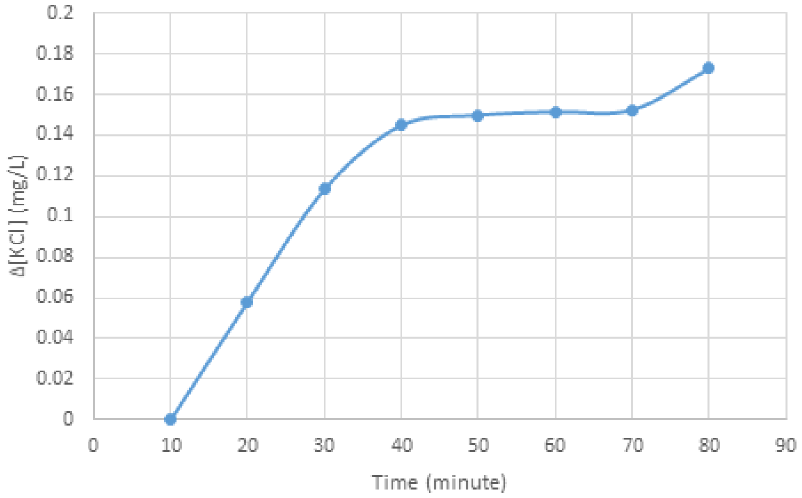

Fig. 6. The increment of potassium chloride release in series of time at the normal period

4. Conclusion

We have successfully prepared a hydrogel based on *glaciallias sp* (GR), poly-(vinyl alcohol) (PVA), glutaraldehyde (GA), and carbon nanotube (CNT), which was called GR/PVA/GA/CNT hydrogel. The FTIR spectra showed that the interaction of hydrogel components involved some functional groups such as C-O, C-N, C=O, C-H sp^3 and O-H which predominantly occurred through hydrogen bonding. Meanwhile, the SEM images indicated that the level of surface roughness increased in the series of GR/PVA/GA, GR/PVA/GA/CNT, and GR/PVA/GA/CNT-K hydrogel. The hydrogel prepared using PVA in technical-grade has a higher swelling ratio compared to that prepared using PVA in pro analytical-grade. The hydrogel showed a typical slow release behavior for potassium ion with the release rate is 8.89 ppm for first ten minutes and the release rate average is 0.0134 ppm/minutes for the normal period. The release mechanism of potassium ions from hydrogel was supposed to begin from the hydrogel surface into bulk, followed by the intrusion of water into hydrogel matrix, which eventually exerted potassium ions from the inner part of hydrogel.

Acknowledgements*. We would like to acknowledge RISTEK DIKTI for supporting the research.*

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