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Characterization of PVA/glycerin hydrogels using γ-irradiation for advanced wound dressings

Hui-Jeong Gwon*,, Youn-Mook Lim*, Sung-Jun An*, Min-Ho Youn*, Seol-Hee Han*, Ho-Nam Chang**, and Young-Chang Nho*,†**

*Radiation Research Center for Industry & Environment, Advanced Radiation Technology Institute, Korea Atomic Energy Research Institute, 1266 Sinjeong-dong, Jeongeup-si, Jeonbuk 580-185, Korea
**Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science Technology, Daejeon 305-701, Korea
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Abstract−The aim of this study was to investigate the enhanced absorption property of PVA/Glycerin (PVA/Gly) hydrogel for advanced wound dressing. A simple crosslinking method was introduced to prepare the PVA/Gly hydrogels with the use of γ-irradiation. An absorption ratio and thermal properties of the PVA/Gly hydrogels can be controlled by varying the irradiation dose and weight ratio of the PVA/Gly. When the PVA/Gly content was 20/5 wt% and the irradiation dose at 25 kGy, the PVA/Gly hydrogels showed excellent absorption properties (>350%). These results imply that the PVA/Gly hydrogel is highly absorbent and converts wound exudates to the hydrogel matrices that create a moist and clean environment in the wound healing process. Therefore, the PVA/Gly hydrogel prepared by this method can be used as an advanced wound dressing.

Key words: Absorption, Gamma Irradiation, PVA/Glycerin Hydrogel, Wound Healing

INTRODUCTION

Hydrogels are three-dimensional hydrophilic polymeric networks that can absorb large amounts of water or a biological fluid without dissolution due to the presence of chemical crosslinks, or physical crosslinks [1,2]. It has been reported that a hydrogel can absorb an excess of wound exudates, protect a wound from secondary infection, and effectively promote the healing process by providing a moisturized wound healing environment [3]. Moreover, these hydrogels are often used as drug delivery systems because of their ability to swell as well as to release the trapped particles into the surrounding medium [4]. An ideal wound dressing should absorb body fluids effectively, be painless for a removal, have a high elasticity, good adhesion and easy replacement, and act as a barrier against bacteria [5,6]. Many commercially available synthetic polymers, such as polyvinyl alcohol (PVA), show physicochemical and mechanical properties comparable to those biological tissues to be substituted [7-11]. These PVA based on hydrogels have received increasing attention in biomedical and biochemical applications, because of their permeability, biocompatibility and biodegradability [12-14]. Therefore, PVA hydrogels have been developed for repair of wounds and promotion of a wound healing [7,15]. Glycerin is a sweet colorless, transparent, and odorless syrupy liquid. It is a humectant, i.e. "draws moisture." It is used in creams, lotions, facial treatments, masks, and other body care products.

To prepare hydrogels, a chemical crosslinking has been reported as one of the crosslinking methods [16]. However, in this method, crosslinking agents such as glutaraldehyde, diisocyanates, carbodiimides and acyl azide are necessary to initiate the process, which reduces their bio-compatibility, due to their inherent cytotoxicity, which also causes further problems with a purification of the final product [17]. γ-Ray irradiation has been recognized as a very suitable method for the formation of hydrogels. Its main advantages, compared to the other methods, are no necessity to add any initiators and crosslinkers to start the process, hence the final product contains only polymer in its structure and the final product does not require a further purification. Moreover, γ-ray irradiation usually allows for the combination of a synthesis and sterilization of polymeric materials in one technological step, thus reducing the costs and production time [18]. These make a γ-ray irradiation a very suitable tool for preparation of hydrogels.

In this study, the poly(vinyl alcohol) (PVA) based hydrogel was prepared by using γ-ray irradiation to simplify the crosslinking process and glycerin was used as a moisturizer to improve the hygroscopic nature. The effects of the irradiation dose, the contents of PVA and glycerin on the absorption ratio and thermal properties were investigated to create the desired hydrogels for an advanced wound dressing.

EXPERIMENT

1. Materials

Poly(vinyl alcohol) (PVA) (Mw=8.5×10^4-1.46×10^5, 98% hydrolyzed) was supplied by the Aldrich Chemical Company (WI, USA). Glycerin was supplied by the Showa Company (Japan). These polymers were used without further purification. Distilled water was used as a solvent in all the experiments. Fig. 1 shows the molecular structures of PVA and glycerin.

2. Preparation of Hydrogels

PVA/Glycerin (PVA/Gly) was dissolved in distilled water at 120 °C

†To whom correspondence should be addressed.
E-mail: ycnho@kaeri.re.kr

(a) (b)

Fig. 1. Chemical structures of (a) poly(vinyl alcohol) and (b) glycerin.

for 20 min by using an autoclave. The contents of PVA in the solution varied from 17.5% to 22.5%. To remove bubbles and prevent the hardening of the homogeneous solutions, the solutions were placed in a water bath at 70 °C for 30 min. These solutions were then poured into Petri dishes and γ-irradiation were performed by ^{60}Co γ-ray to doses of 25 kGy at a dose rate of 10 kGy/h.

3. Gel Content

The gel content of the hydrogels was measured by extraction in hot distilled water at 50 °C for 48 h and drying in vacuum at 50 °C for 48 h until they reached constant weight. The gel content (G_c) was defined gravimetrically by G_c (%)=(W_d/W_i)×100. Where W_d is the oven-dried gel weight after the swelling for 48 h, and W_i is the initial weight of the dried hydrogels.

4. Absorption Ratio

The hydrogel samples were immersed in distilled water for different times at room temperature until an equilibrium state of absorption was achieved. After the excessive surface water was removed with filler paper, the weight of the swollen gel was measured at various time intervals. The procedure was repeated until there was no further weight increase. The swollen gels were then dried at 60 °C for 48 h to a constant weight. The ratio of absorption (D_s) of the hydrogels was given by D_s (%)=[(W_s−W_d)/ W_i]×100. Where W_s is the weight of the swollen gels, W_d is the oven-dried gel weight after the swelling test, and W_i is the initial weight of the dried hydrogels.

5. Thermal Analysis

The hydrogel samples were dried at 60 °C for 48 h before differential scanning calorimetry (DSC, DSCQ100 TA Instrument Company). During a measurement, the extracted dry hydrogels were heated from 30 to 240 °C under N_2 atmosphere with a heating rate of 10 °C/min.

RESULTS AND DISCUSSION

1. Characterization of PVA/Gly Hydrogels

The radiation technique is a very convenient tool for the improvement or modification of polymer materials through cross-linking, grafting, or degradation. The radiation-crosslinked PVA/Gly hydrogels were successfully prepared and showed the excellent or equivalent swelling behavior and mechanical properties for advanced wound dressing. Crosslinking by radiation transforms a linear polymer into a three-dimensional molecule, resulting in a significant increase in the molecular mass, lower solubility in organic solvents, and improved mechanical properties. Degradation results in a decrease in the molecular mass, and has the opposite effect on the physical properties of the polymer. Crosslinking and degradation occur simultaneously. However, the ratio of their rates depends on the chemical structure of the polymer, its physical state, and the irradiation state. Polymers are generally divided into those that predominantly crosslink and those that predominantly degrade.

Table 1. The melting temperatures (°C) for PVA/Gly hydrogels at different compositions

Irradiation dose (kGy)	PVA/Gly content (wt%)					
	17.5/5	17.5/10	20/5	20/10	22.5/5	22.5/10
15	189.9	190.1	195.8	195.2	201.1	200.7
25	188.4	189.2	193.9	193.5	198.9	198.6

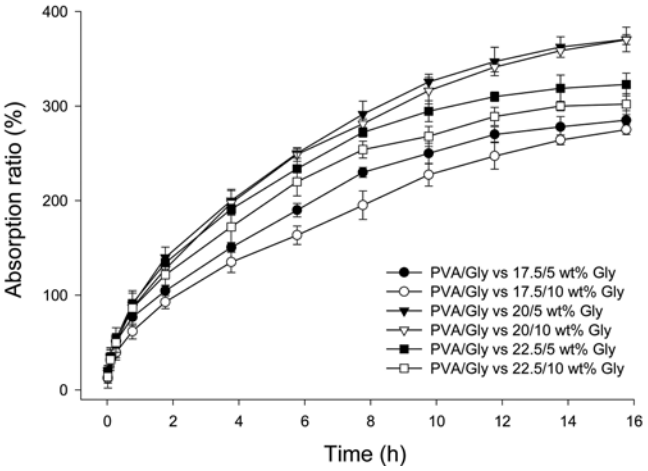

Fig. 2. The absorption ratio as a function of the content of PVA/Gly.

Table 1 shows the gelation behavior of the PVA/Gly hydrogels. The gel content increased as the concentration of the PVA increased, while the gel content slightly decreased as the concentration of the glycerin increased. These results were due to the increase of the crosslinking density of PVA, and the increased glycerin concentrations led to decrease the weight ratio of PVA in the hydrogels.

Fig. 2 shows the absorption ratio of the hydrogels as a function of the PVA and glycerin contents and absorption time. The ability of hydrogel to absorb and hold significant amounts of solvent inside their network structure is one of their most important features. This absorption ability is an important parameter for its practical uses, such as a wound dressing. These hydrogels should have large water absorption capacity in order to absorb wound exudates, and this absorption property makes those hydrogels a suitable material as a wound dressing. In this study, the absorption ratio of PVA/Gly hydrogel in distilled water was investigated. The absorption curves show a similar shape but differ in size and position, and the absorption ratio sharply increases and then begins to level off. The hydrogels made from the 20/5 wt% concentration of PVA/Gly showed an excellent absorption ratio with 350%. It was seen from Fig. 2 that the absorption ratio increased with increasing the content of PVA/Gly due to their high hydrophilicity, but decreased when the PVA/Gly content increased above 20/5 wt%. This is probably due to an increase in the crosslinking density for larger PVA contents.

The thermal properties of the hydrogels were studied by DSC measurements. Table 2 and Fig. 3 present the melting temperatures of the hydrogels prepared by using γ-irradiation. The pure PVA has

Table 2. The gel content (%) of PVA/Gly hydrogels at different compositions

Glycerin content (wt%)	PVA content (wt%)		
	17.5	20	22.5
0	91.3	92.3	93.5
5	89.8	91.8	92.8
10	88.3	90.4	91.1

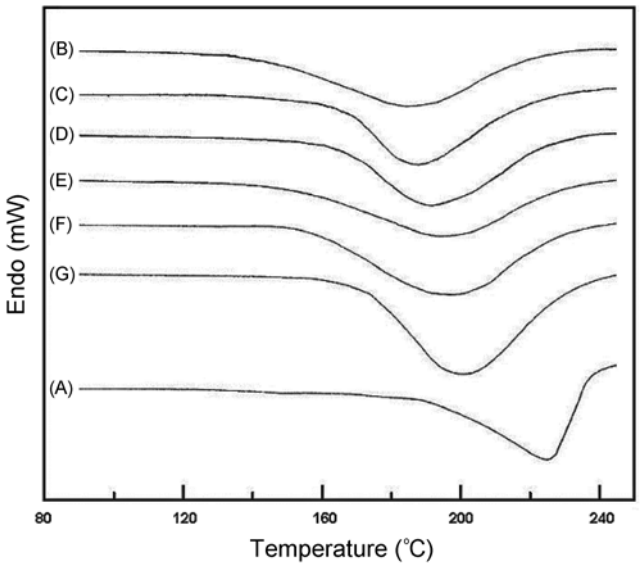

Fig. 3. The DSC curve of PVA/Gly hydrogel at different compositions. (A): pure PVA, (C), (E) and (G): the content of PVA/Gly are 17.5/5, 20/5 and 22.5/5 at 15 kGy, respectively. (B), (D) and (F): the content of PVA/Gly are 17.5/5, 20/5 and 22.5/5 at 25 kGy, respectively.

an endothermic peak at about 227.8 °C, corresponding to the melting points of PVA. The melting temperature is reduced for the PVA/Gly blends and it decreases with decreasing PVA content. This indicates that the ordered associations of PVA molecules are decreased by the presence of glycerol. An increase in the irradiation dose results in a reduction in the melting temperature. This is probably due to the morphological and chemical changes. The morphological changes involve the thickness of the crystallites and the degree of crystallinity. The chemical changes formed by irradiation often involve the crosslinking and degradation, and these changes often decrease the degree of crystallinity with increasing irradiation dose. The chemical changes formed by irradiation thus reduce the melting temperature. Therefore, it can be seen that irradiation influenced the thermal behavior of PVA.

CONCLUSION

To enhance their absorption properties, PVA/Gly hydrogels were developed by using a γ-irradiation technique without any additives. The hydrogels were investigated for the effects of the irradiation doses, and the content of PVA and glycerin on their absorption ratio and thermal properties. The most efficient crosslinking conditions were obtained for the PVA/Gly content of 20/5 wt% at 25 kGy and these hydrogels which can provide an excellent absorption ratio (>350%) for an application. These results imply that the PVA/Gly hydrogel prepared by this method has a potential for advanced wound dressing and further studies will be done to support this study.

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