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Preparation of PVP/MHEC Blended Hydrogels via Gamma Irradiation and Their Calcium ion Uptaking and Releasing Ability

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Abstract

The present work was aimed to prepare hydrogels from polymer blend between poly (\textit{N}-vinyl pyrrolidone) (PVP) and methyl hydroxyethyl cellulose (MHEC) via \textsuperscript{60}Co gamma irradiation. The crosslinking structures in the hydrogels were induced by varying the irradiation doses from 10 to 40 kGy. The gel fraction and the swelling ratio of hydrogels were characterized. The results showed that the swelling ratio of hydrogels increases with increasing the irradiation dose while the gel fraction of hydrogels depended on the obtained hydrogels prepared from PVP or MHEC. The hydrogels were determined the calcium ion uptaking and releasing ability in the water.

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Keywords: Gamma irradiation ; Hydrogels ; Poly (\textit{N}-vinyl pyrrolidone) ; Methyl hydroxylethyl cellulose ; Calcium ion

1. Introduction

Hydrogels or aquagels are the well known as crosslinked polymers, which have performed the high water adsorption and swell as well (Scheme 1). Due to their properties, the hydrogels have received much

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attention for used widely in the large fields, such as a matrix for drug delivery, oil adsorption, scaffolds in tissue engineering, and etc. [1-6].

The network structure of hydrogels was prepared by the radiation-induced method from cross-linking agent and various polymers, such as poly vinyl alcohol (PVA) polyethylene oxide (PEO) cellulose and etc. [1-5].

Poly (N-vinyl pyrrolidone) (PVP) hydrogel is synthetic polymer with good biocompatibility and transparency. However, the properties of PVP hydrogel such as fragility, especially water swelling need to be improved further for hydrogel applications. PVP hydrogel can get improved properties by blending with other polymers such as polysaccharides or carboxymethyl cellulose (CMC) [1-4, 6].

Methyl hydroxyl ethyl cellulose (MHEC, also called HEMC) is a natural polymer derived from cellulose. Generally, The MHEC is a hydrophilic white powder and dissolves easily in cold water, forming a clear viscous solution and gel. Although the MHEC has many advantages such as water solubility, biocompatibility and nontoxic but MHEC hydrogel shows very poor mechanical strength and swollen form. The applications of MHEC hydrogel are consequently limited [6].

From the reasons above, we synthesized a PVP/MHEC blend hydrogels via $^{60}$Co γ-ray irradiation to overcome their poor properties. The blended hydrogels were determined the gel fraction and swelling in water. In addition, the calcium ions uptaking and releasing ability in the water of the absorbing hydrogels was investigated for applying to solve a sodic soil problem in the future.

2. Experimental

2.1. Materials

Poly (N-vinyl pyrrolidone) (PVP) with a molecular weight of ~ 40,000 was purchased from MERCK (Germany). Methyl hydroxyethyl cellulose (MHEC, Tylose MH 60001 P6) was purchased from Shin Etsu (Germany). Calcium nitrate tetrahydrate (CaCO$_3$.4H$_2$O) and absolute ethanol were obtained from AnalR (Thailand).

2.2. Instruments

All compounds were weighed with a balance (AB204-s/FACT METTLER). The obtained hydrogels were synthesized by $^{60}$Co γ-ray irradiation from GC-5000 Gamma Chamber. All swollen hydrogels were dried with a Carbolite oven (2416 temperature control). The UV-Visible absorption of all solutions was measured with a Shimadzu Pharmaspec UV-1700 spectrophotometer in a wavelength of 301 nm.
2.3. Preparation of PVP-MHEC blended hydrogels via gamma ray irradiation

Various compositions of PVP, MHEC and distilled water (Table 1) were mixed and then heated on a hot plate at 80°C for 20 min to obtain the solutions of PVP and MHEC.

The obtained solutions were poured into plastic bags, sealed and irradiated by $^{60}$Co gamma radiation with various doses of 20-40 kGy. The irradiated samples were cut in pieces 1x1 cm and dried in oven at 60°C for 48 h.

Table 1. The compositions of starting materials for MHEC/PVP blended hydrogels preparation

<table>
<thead>
<tr>
<th>MHEC/PVP blended hydrogels</th>
<th>Weight (g)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PVP</td>
<td>MHEC</td>
<td>Water</td>
</tr>
<tr>
<td>HG1</td>
<td>7</td>
<td>13</td>
<td>80</td>
</tr>
<tr>
<td>HG2</td>
<td>6</td>
<td>14</td>
<td>80</td>
</tr>
<tr>
<td>HG3</td>
<td>5</td>
<td>15</td>
<td>80</td>
</tr>
<tr>
<td>HG4</td>
<td>4</td>
<td>16</td>
<td>80</td>
</tr>
<tr>
<td>HG5</td>
<td>3</td>
<td>17</td>
<td>80</td>
</tr>
</tbody>
</table>

2.4. Determination of gel fraction and gel swelling

The dried hydrogels were weighed and wrapped in 4x4 cm sieve and then extracted in hot distilled water at 80°C for 1 h to determine the gel fraction (%Gel fraction). After extraction, the hydrogels were collected and soaked in ethanol for 15 min, dried in the oven at 60°C for 48 h. The dried gels were then weighed to determine the gel content that was defined as the equation (1): where $w_d$ is the weight of the dried gel after extraction, $w_s$ is the weight of the sieve and $w_i$ is the initial weight of the dried gel.

$$\% \text{Gel fraction} = \frac{(w_d - w_s)}{(w_i - w_s)} \times 100$$  \hspace{1cm} (1)

All dried gel samples were weighed and immersed in distilled water for 72 hours at room temperature to determine the degree of swelling (DS) or the water absorption of the hydrogels. The DS value is defined as the equation (2): where $w_s$ is the weight of the swollen gel and $w_d$ is the dried gel weight.

$$\text{DS} = \frac{(w_s - w_d)}{w_d} \times 100$$  \hspace{1cm} (2)

2.5. Determination of calcium ion uptaking and releasing ability

To determine the calcium ion uptaking and releasing ability, the dried hydrogels irradiated at 30 kGy of the PVP-MHEC blended were soaked in various calcium nitrate solutions at concentrations of 10, 15, 20, and 30 weight percentages for 72 h and then dried in the oven at 60°C for 48 h.

The calcium nitrate uptake fractions of PVP-MHEC blended hydrogels were defined by the ratio of dried weight of hydrogels with calcium nitrate and initial dried weight of hydrogels (equation (3)): where $w_{fc}$ is the weight of dried gel before soking in the calcium nitrate solution and $w_{ic}$ is the dried gel after soking in the calcium nitrate solution.

$$\text{Calcium uptake fraction} = \frac{(w_{fc} - w_{ic})}{w_{ic}} \times 100$$  \hspace{1cm} (3)
To determine the calcium ion releasing ability, the PVP-MHEC blended hydrogels were soaked in the distilled water for 30 h. The calcium ion releasing abilities of the PVP-MHEC blended hydrogels were examined by a UV-visible spectrophotometer at 301 nm for every 1.5 h (for 6 h) and in next 24 h.

The calcium ion releasing ability was calculated from the concentration of the calcium ions after releasing from the PVP-MHEC blended hydrogels to the distilled water.

3. Results and discussion

3.1. Gel fraction and gel swelling of PVP-MHEC hydrogels

By irradiating $^{60}$Co gamma radiation from 10-40 kGy, the PVP-MHEC aqueous solutions leaded to form the insoluble polymer network (gel). The results of the gel fractions of the PVP-MHEC blended hydrogels shown in Fig. 1 indicated that the irradiation dose increased with decreasing the gel fraction of the PVP-MHEC hydrogels.

The optimum irradiation dose for gel fraction of PVP-MHEC hydrogels was also found to be 20 kGy. This result also agreed with that from gel swelling at different irradiation doses in Fig. 2. Although the gel swelling of hydrogel was the highest at 10 kGy, the gel formation was not stable. In addition, it might be the fact that the crosslink formation of both PVP and MHEC was inhibited and decomposed at higher gamma radiation than 20 kGy.

![Fig. 1. Irradiation doses for gel fraction of PVP-MHEC blended hydrogels](image1)

![Fig. 2. Irradiation doses for gel swelling of PVP-MHEC blended hydrogels](image2)
The swelling kinetics (Fig. 3) of PVP-MHEC blended hydrogels were also determined. It was found that the crosslinking density of PVP-MHEC blended hydrogels increases with decreasing swelling rate.

By considering the results in Figure 3, it was found that the samples provided the highest water adsorption and gel swelling were HG-3, HG-4 and HG-5, respectively. Therefore, these three samples were selected to study the calcium ion uptaking and releasing ability.

3.2. Gel fraction and gel swelling of PVP-MHEC hydrogels

The HG-5 hydrogel exhibited the calcium ion uptaking percentage as comparing with HG-3 and HG-4 hydrogels. This indicated that the calcium ion uptaking ability depended on the gel fraction and gel swelling of the PVP/MHEC hydrogels. It might be the fact that among of three hydrogels (HG-3, HG-4 and HG-5), the crosslink density of the HG-5 was found to be the lowest.
The releasing ratios of PVP/MHEC hydrogels were compared and shown in Fig. 5. From the results, the HG-5 hydrogel showed the greatest releasing ability in 0.5 h as comparing with other hydrogels (HG-3 and HG-4). However, in practical, the ion releasing rate should be low to avoid the fast elution of calcium ions in soil by water. The HG-5 was not soluble for using in practical even it has the highest calcium uptake percentage. Therefore, HG-3 and HG-4 hydrogels were considered.

From Fig. 5, the results illustrated that the rates of releasing density of HG-3 and HG-4 hydrogels are low at the initial (0.5 h) and increased with time after 0.5 h. However, the rate of releasing ability of the HG3 hydrogel has slower than that of the HG-4. It might be the fact that the HG-3 has the highest crosslink density. After the dried gel of the HG-3 was added into the water, it requires the swelling time for gels to release calcium ions. Therefore, it can be concluded that the HG-3 is the most useful in practical for sodic soil remedy.

4. Conclusion

PVP and MHEC hydrogels with different compositions have been successfully prepared via gamma radiation. The optimized irradiation dose for PVP-MHEC hydrogels is 20 kGy. The crosslink formation of PVP and MHEC were inhibited and decomposed at higher than 20 kGy of gamma radiation. In this work, the HG-3 was found to be a suitable hydrogel to apply in the sodic soil remedy while the calcium ion releasing ability to soil will be further studied in near future.

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References


