UV IRRADIATION FORMATION OF POLY(VINYL ALCOHOL)/CHITOSAN HYDROGEL THIN FILMS FOR BIOMEDICAL APPLICATION

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Abstract - The work presented herein aimed to investigate and fabricate a series of poly (vinyl alcohol) (PVA)/Chitosan (CTS) hydrogel thin films by ultraviolet (UV) irradiation method using acrylic acid (AAc) monomer as a crosslinker, without adding any photoinitiator. The effect of reaction conditions such as the concentration of AAc and the irradiation time were investigated by Fourier Transform Infrared (FTIR), X-Ray Diffraction (XRD), and Scanning Electron Microscope (SEM). FTIR spectra confirmed that poly(acrylic acid) (PAAc) was polymerized successfully and the chemical crosslink was formed in hydrogel film. XRD analyses indicated that the crystalline degree of the hydrogel film decreased with the increase of the PAAc content. SEM micrographs showed the uniform interconnected pore formation through the entire hydrogel structure and the gradient in crosslink density through the film thickness was observed by extent irradiation time. With the increase of UV irradiation time, hydrogel thin films remained the interlinked pores in the interior and showed the larger inter-pores on the surface. The prepared transparent and thin PVA/CTS hydrogel thin film for biomedical applications.

Keywords: Poly(vinyl alcohol); Chitosan; Ultraviolet irradiation; Hydrogel thin films; Biomedical applications.

Introduction
Hydrogels known as cross-linked polymeric networks that are able to adsorb water without dissolving, have been extensively used in a variety of biomedical applications due to their unique biocompatibility, flexible methods of synthesis, range of constituents, and desirable physical characteristics [1-2]. They can be fabricated by many methods such as irradiation, thermal annealing, freeze-thawing, as well as by using crosslinking chemical agents to generate the physical or chemical crosslinked hydrophilic polymer networks. In which irradiation (e.g. γ-rays, electron beam, or UV irradiation) is considered as an effective tool [3-7]. By using of UV irradiation to crosslink or chemically modify polymer systems, a photoinitiator and a crosslinker are usually used to induce free radicals for covalent crosslinking performance. Most of the crosslinkers and chemical initiators are toxic and difficult to remove from polymer networks; and only a free trace of them may be a harmful factor for biomedical-related applications [8]. To overcome this shortcoming, a desired route is choosing proper monomers which directly form free radicals by adsorption of UV irradiation. In this work, acrylic acid monomer was employed as a crosslinker to fabricate poly(vinyl alcohol)/chitosan hydrogel thin films via ultraviolet (UV) irradiation without using photoinitiator or additional crosslinking agents.

Experimental

1. Material
PVA (Mw=145 000, fully hydrolysis) was obtained from Merck. Chitosan (Mw = 100 000 ÷ 300 000, deacetylation ≥ 85 %) and acrylic acid were purchased from Acros Organics. Deionized (DI) water from a Millipore-Q system was used as the solvent in all experiments. All chemicals were used as received except that AAc was vacuum distilled to remove the polymerization inhibitor before use.

2. Preparation of the hydrogel thin films
PVA/CTS hydrogel thin films were prepared by UV irradiation by which crosslinked PAAc chains were formed in the hydrogel. The feed composition and designation of the films are listed in Table 1. The homogeneous solutions were casted onto Petri dishes and exposed to a 1000 W UV lamp (1000 UV curing, Taiwan) with a wavelength range of 250 ÷ 420 nm, at a distance of 15 cm, under nitrogen atmosphere. The result films of 45 ÷ 5 μm in thickness were characterized by FTIR (Jasco VALOR III), XRD (Rigaku Ultima IV XRD) and SEM (JEOL HRFESEM JSM-6700F).

Results and Discussion

1. FTIR
Fig. 1 shows FTIR spectra of PVA, CTS, PAA 20-30 and S23-30. The absorption bands of C=O in PAAc are located at 1766 cm⁻¹. This band for S23-30 hydrogel is shifted to a lower frequency of 1720 cm⁻¹ with high intensity indicating that a strong hydrogen bonding and

Table 1. The feed composition and designation of the PVA/CTS thin films

<table>
<thead>
<tr>
<th>Code a</th>
<th>Molar ratio [OH]+[NH₂]/[COOH]</th>
<th>Weight (gram)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S20-xx b</td>
<td>2: 0</td>
<td>0.5</td>
</tr>
<tr>
<td>S21-xx</td>
<td>2 : 1</td>
<td>0.5</td>
</tr>
<tr>
<td>S22-xx</td>
<td>2 : 2</td>
<td>0.5</td>
</tr>
<tr>
<td>S23-xx</td>
<td>2 : 3</td>
<td>0.5</td>
</tr>
</tbody>
</table>

a 5 wt % of PVA and 2 wt % of CTS was prepared for all solutions.

b The irradiation times were 15, 30 or 45 min, respectively.

c 3 wt % of acetic acid was used to dissolve CTS.
also electrostatic interaction should occur among PVA, CTS and PAAC in this hydrogel. The ionization of primary amino group of CTS in the presence of carboxylic group of PAAC can be observed around 1544 cm\(^{-1}\) due to symmetric deformation of \(-\text{NH}_3^+\) [9]. In contrast, the C=O stretching band of S20-30 hydrogel is located at 1710 cm\(^{-1}\) with low intensity even an equivalent amount of acetic acid compared with AAc monomer to dissolve CTS has been used. On the other hand, after extracting S23-30 hydrogel for 72 hrs at 50°C in DI water, a high intensity of the C=O band located around 1720 cm\(^{-1}\) confirmed that the AAc has been polymerized and crosslinked under UV irradiation [10].

2. XRD
The X-ray diffraction patterns of PVA, CTS, PAAC and various PVA/CTS hydrogel thin films after 30 min UV irradiation are showed in Fig. 2. The characteristic peaks of PVA are located at \(\theta = 11.4^\circ, 19.7^\circ, 22.9^\circ\) and \(41^\circ\) while those of CTS are exhibited at \(\theta = 10.6^\circ\) and \(19.6^\circ\). On the other hand, diffraction pattern of PAAC does not show any peaks indicating that it is totally amorphous [6]. As showed in Fig. 2d-2g, the effect of the PAAC content in the crystallinity of the result films are obtained obviously. Two peaks for the various hydrogel films are found: One peak with high intensity appears at \(\theta = 19.7^\circ\) and another peak with very low intensity appears at \(\theta = 41^\circ\). With increasing the content of PAAC in the hydrogel, the relative intensity of the peaks decreases significantly. It can be explained that the decrease in crystallinity of these hydrogel films are attributed to the deformation of the strong hydrogen bonding between hydroxyl and amino groups in both CTS and PVA due to interaction of these groups with carboxyl groups of PAAC, as well as the formation of PAAC network in the hydrogel films. Similar discussions for the deformation of crystal structure had been reported in several references [11-13].

3. SEM
The effect of irradiation time on the surface and cross-section morphologies of PVA/CTS hydrogel thin films are obtained obviously in Fig. 3. All the hydrogels exhibit an interlinked pore structure, however, the pore size seems to be increases with extending of irradiation time. As can be seen in Fig. 3, after 15 and 30 min UV irradiation, the interconnecting pores are observed through the entire hydrogel structure; however, the surface image shows lager inter-pores of the 30 min irradiated hydrogel film. After 45 min irradiation, the top surface of the thin film shows a dense, noporouse structure while the interlinked pores are still remained inside hydrogel film. It indicates that the microstructure of hydrogels film is strong effect by the irradiation time. These changes in morphology of hydrogel can be explained by the formation of PAAC and its crosslinked network in hydrogel film. It is known that, PAAC has the excellent water swelling property, thus, the more PAAC content in the film, the higher water retaining in the hydrated hydrogel and as a result, the larger pore size will be after lyophilization [14].

It is reported that PAAC, like most polymers, was degraded when exposed to the 254 nm UV irradiation in the presence of oxygen containing atmosphere [15-17]. In this case, the hydrogel thin film that was obtained by UV irradiation for 45 min in a nitrogen atmosphere is dense in the surface and loose in the interior because chemical crosslinking at surface is more dominant than that inside the hydrogel film. The results clearly exhibited that a gradient in crosslink density exists through the film thickness even though it is in microscale. The porous structure and biocompati-
Figure 3. SEM micrographs of the surface and cross-section of various PVA/CTS hydrogel films containing same composition and made by different UV irradiation times: (a) S23-15, (b) S23-30 and (c) S23-45.

Conclusions
A series of PVA/CTS hydrogel thin films were synthesized by using AAc monomer as a crosslinker under UV irradiation without using photoinitiator or addition of crosslinking agents. The properties of these films including chemical bonds, molecular structure, crystallinity degree, the morphology of the surface and internal structure, as well as their relationship to AAc content were studied by FTIR, XRD and SEM analysis. It is found that PAAc had been polymerized and chemical crosslink was formed in the hydrogel film. By this approach, PVA/CTS hydrogel thin film can be used as biomaterial for medical applications because of its inherent biocompatible and purity.

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References
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