



# Critical review of radiation processing of hydrogel and polysaccharide

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## ABSTRACT

Radiation processing of an aqueous solution of polymer initiated by  $\bullet\text{OH}$  radicals formed by radiolysis of water is applied for preparation of hydrogel wound dressing and plant growth promoter. Recently, Fenton reagent that generates  $\bullet\text{OH}$  radicals was successfully applied to synthesize PVP hydrogel. The Fenton reaction also can be applied to the depolymerization of chitosan. These progresses in the syntheses of hydrogel and oligo-chitosan by radiation and non-radiation methods such as hydrolysis, oxidative degradation, photolysis, sonolysis and degradation by microwave are reviewed to survey a possibility to reduce the costs of production. Radiation synthesized hydrogel should target value-added medical products because only radiation can crosslink and sterilize simultaneously. Oligo-chitosan can be produced economically by irradiation of solid chitin by Fenton reagent, if necessary.

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## 1. Introduction

Syntheses of hydrogel and oligo-chitosan by radiation are the major R&D subjects in many radiation processing laboratories of nuclear research institutes. Hydrogel is prepared by irradiation of an aqueous solution of polymer and the oligo-chitosan is produced by radiation degradation of chitosan in an aqueous solution. The main application of radiation-processed hydrogel is wound dressing at present time. Applications of radiation-processed hydrogel for treatment of agro wastes such as cattle waste and fermentation residue have been attempted. The radiation processed hydrogel is too costly to use in agriculture. A few alternative methods are investigated for preparation of hydrogel. For example, Fenton reagent that generates  $\bullet\text{OH}$  radicals chemically is successfully applied for synthesis of PVP hydrogel. Similarly, there are several methods for the degradation of chitosan and Fenton reagent also can be applied to the degradation of chitosan. In this paper, recent progress in crosslinking of PVP and degradation of chitosan in aqueous solution is reviewed from an energy consumption standpoint.

## 2. Hydrogel

Rosiak and coworkers commercialized hydrogel wound dressing by radiation crosslinking of polymers in aqueous solution in 1990. The wound dressings were composed of poly(vinyl pyrrolidone), poly(ethylene glycol), agar and water. The dressings in the final form are transparent sheets of few millimeters thickness and different dimensions, containing over 90% water.

The first step of manufacturing is the preparation of an aqueous solution of dressing's components. After dissolving and mixing them at elevated temperature, a homogenous solution was formed. Then the moulds, which can also be used as final packages, were filled with liquid solution of the dressing components. After cooling down, the solution becomes physically solid gels (high viscous), which then is packed in the proper final boxes. The packages of solid gels were finally exposed to  $\gamma$ -rays at a dose rate of 6 kGy/h to become crosslinked (Rosiak and Olejniczak, 1993). Usually a dose of 25 kGy is applied in order to ensure sterility of the product (Ajji et al., 2005).

The primary process involved in radiation synthesis of hydrogel is formation of hydroxyl radicals by water radiolysis. The hydroxyl radical ( $\bullet\text{OH}$ ) reacts with polymer in aqueous solution to generate polymer radical that combines with each other, resulting in crosslinking of polymers (Rosiak, 1991). For biomedical applications, hydrogel produced by crosslinking the polymers in aqueous solution is preferred since no residual monomer is left as a potential toxic agent. In addition, simultaneous synthesis and sterilization of hydrogel are the unique advantage of radiation processing. The process is so simple that several similar hydrogel wound dressings have been developed and commercialized in Asian countries as shown in Table 1.

Recently, non-radiation methods for PVP hydrogel have been developed. Since PVP in aqueous solution absorbs UV in the region of 200–280 nm, direct photocrosslinking of PVP occurs by the UV irradiation with low pressure Hg lamp (Lilian et al., 2003). Hydrogel by direct photocrosslinking of agar, polyethylene glycol (PEG 300 and 400) and chitosan showed a good performance and appearance (Felinto et al., 2007). Hydrogen peroxide is added to the direct photocrosslinking system to enhance the crosslinking efficiency (Barros et al., 2006). The photolysis of  $\text{H}_2\text{O}_2$  generates  $\bullet\text{OH}$ , the same species responsible for radiation crosslinking of

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**Table 1**  
Commercialization of radiation-processed hydrogel for wound dressing.

Developed by	Produced by	Trade name	Marketed year	Main composition
KAERI JAEA	Hyundai Pharmaceutical Nichiban	Cligel	2004	PVP/CR/PEG
		VIEWGEL Gel protector	2004	PVA
China Institute of Atomic Energy BARC	Changchun JA Biotech. ABS Medicare Dr. Reddy's Labo.	Burn Caring	2005	PVA/PVP/Agr
		HiZel	2006	PVA/Agr/CR
		Hydroheal	2006	

PVA: poly(vinyl alcohol), CR: carrageenan.

**Table 2**  
Comparison of energy consumption for production of PVP hydrogel.

Method	Ingredients	Radiation source	J/g
Radiation <sup>a</sup>	PVP:Agar:PEG	$\gamma$ -rays, 6 kGy/h	25
Radiation <sup>b</sup>	PVP:Agar:PEG=8:1.5:1 [%]	Dynamitron 1.5 MeV, 11.3 kGy/s	25
Direct UV <sup>c</sup>	PVP [80 g/L]	UV, $\lambda$ =254 nm	207
Direct UV <sup>d</sup>	PVP [80 g/L]	UV, $\lambda$ =254 nm	242
Sensitized UV with H <sub>2</sub> O <sub>2</sub> <sup>d</sup>	PVP:H <sub>2</sub> O <sub>2</sub> =80 g/L:10 mmol/L	UV, $\lambda$ =254 nm	40
Sensitized UV with Fe <sup>3+</sup> and H <sub>2</sub> O <sub>2</sub> <sup>d</sup>	PVP: H <sub>2</sub> O <sub>2</sub> :Fe <sup>3+</sup> = 80 g/L:50 mmol/L:5 mmol/L	UV, $\lambda$ =360 nm	114
Fenton, Fe <sup>2+</sup> and H <sub>2</sub> O <sub>2</sub> <sup>e</sup>	PVP: H <sub>2</sub> O <sub>2</sub> :Fe <sup>2+</sup> = 80 g/L:50 mmol/L:5 mmol/L, pH=2.5	None	

<sup>a</sup> Rosiak and Olejniczak, 1993.

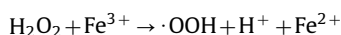
<sup>b</sup> Higa et al., 1999.

<sup>c</sup> Lopergoloa et al., 2003.

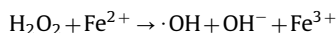
<sup>d</sup> Fehine et al., 2004.

<sup>e</sup> Barros et al., 2006.

PVP in water. Consequently, energy consumption is reduced one order lower than the direct photocrosslinking. This sensitized photocrosslinking was applied to co-crosslinking between PVP and poly(acrylic acid) (PAA) (Kadlubowski et al., 2007)). Addition of Fe<sup>3+</sup> to the UV-H<sub>2</sub>O<sub>2</sub> is not effective for the enhancement of the photocrosslinking of PVP (Barros et al., 2006). This is probably due to the weak oxidative reactivity of •OOH radical generated by the following reaction:



Finally, high efficiency crosslinking of PVP was achieved by the Fenton reagent without UV irradiation (Barros et al., 2006). The Fenton reaction, which is a redox reaction generating very strong oxidizing •OH radical, is as follows:



When the two PVP solutions, one containing H<sub>2</sub>O<sub>2</sub> and another containing FeCl<sub>2</sub> are mixed, •OH radicals are formed and the crosslinking of PVP occurs spontaneously within 5–10 s, resulting in the formation of hydrogel.

The cytotoxicity tests showed that hydrogels prepared by these methods do not impose any toxic effect. In addition, all samples presented inflammation indexes within a satisfactory range, i.e., as a non-irritating material. Polyethyleneimine nanogels were prepared from polyethyleneimine pre-polymer by photo-Fenton reaction (Xu et al., 2007).

Table 2 shows the comparison of energy consumption for production of PVP hydrogel by different methods to obtain similar physical properties such as gel content (around 85%), swelling ratio and mechanical properties.

The Fenton method can be applied to other water-soluble polymers for preparation of hydrogel. The Fenton reaction is so rapid that various measures would be developed to apply this method in the industry. The advantage of the radiation processing of hydrogel is the simultaneous crosslinking and sterilization. Thus, radiation-processed hydrogel will be used for the products that need sterilization.

### 3. Oligo-chitosan

Several methods have been reported on the decomposition of polysaccharides as follows:

- Hydrolysis  
Hot water, catalyzed by enzyme, acid and alkali
- Radiolysis  
 $\gamma$ -rays, electron beams,  $\gamma$ -rays/H<sub>2</sub>O<sub>2</sub>,  $\gamma$ -rays/Potassium persulfate (KPS)
- Degradation by microwave
- Photolysis
- Sonolysis
- Oxidative degradation  
H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>/Cu<sup>2+</sup>, H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup>, H<sub>2</sub>O<sub>2</sub>/UV, H<sub>2</sub>O<sub>2</sub>/microwave, Ascorbic Acid/Cu<sup>2+</sup>, Ascorbic Acid/Fe<sup>2+</sup>, KPS persulfate (KPS)

Scission of the glycosidic is the main route of depolymerization. Generally, the degradation rates depend on the concentrations of reactants and temperature, like other chemical reactions. In addition, the rates depend on the purity, degree of deacetylation and molecular weight of chitosan. The hydrolysis of chitosan is catalyzed by enzyme, acid and alkali. The oxidative degradation is initiated mainly by •OH radicals. Hydrogen peroxide is a typical additive to initiate oxidative degradation of chitosan. Photolysis and sonolysis are handy processes to decompose the chitosan in aqueous solution. However, the energy consumptions of both processes are high compared with radiolysis. The microwave process is a kind of pyrolysis at moderate temperature. The energy utilization efficiency of microwave process is very low. Combinations of hydrogen peroxide with radiolysis, photolysis, sonolysis and microwave are tried to enhance the depolymerization of chitosan.

Degraded low molecular weight chitosan (oligo-chitosan) is commercially produced by enzymatic depolymerization of

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