

• 研究论文 •

STUDY OF IRRADIATION GRAFT OF POLY (ETHYLENE OXIDE) HYDROGEL FILMS

YANG Zhanshan

(Suzhou Medical College, Suzhou 215007)

YOSHII Fumio MAKUUCHI Keizo

(Takasaki Radiation Chemistry Research Establishment, Japan Atomic Energy Research Institute, Japan)

ABSTRACT In order to obtain a more ideal hydrogel wound dressing, PEO graft hydrogel films formed by electron beam(EB) irradiation of the aqueous solutions of poly(ethylene oxide) (PEO) incorporated with poly(vinyl alcohol) (PVA) at different ratio were prepared, and their physiochemical properties were investigated as a function of production factors combination. The experimental results showed that gel fraction of the PEO graft hydrogel films depended mainly on irradiation dose and concentration of the polymers. Their degree of swelling was intimately related to irradiation dose, concentration, blending ratio and molecular weight of the polymers. Their tensile strength and elongation at break were obviously dependent on irradiation dose and blending ratio of the polymers. It is found that a new PEO E-30 graft hydrogel film of 20 wt% at a ratio of 7:3 has better physiochemical properties such as flexibility, moderate gel fraction, degree of swelling and elongation at break, especially its higher tensile strength than other PEO graft hydrogel films or pure PEO E-30 hydrogel film. These results indicated that PVA can improve the mechanical strength of the PEO E-30 hydrogel film through reducing the degree of swelling of the PEO E-30 hydrogel film after the irradiation graft.

KEYWORDS Poly(ethylene oxide), Poly(vinyl alcohol), Hydrogel, Property, Radiation graft

1 INTRODUCTION

A great deal of interest has centred upon polymer hydrogels because of their many excellent properties as biomedical materials such as biocompatibility, absorbability, permeability to water vapour and oxygen and controlled release of drugs incorporated in the hydrogels etc. The hydrogels are non-toxic, non-carcinogenic and fully sterile.^[1] PEO hydrogels have proved very useful in the treatment of scalds on children and partial burns^[2]. PVA hydrogels also are widely used as biomedical materials^[3,4,5]. However, one of the major problems in the application of these materials is their relatively poor mechanical strength. The mechanical properties are highly dependent on the polymer structure, especially the cross-linking density and the degree of swelling^[1,6].

If the hydrogel is not a homopolymer, then increasing the relative amount of physically stronger components will lead to an increase in the mechanical strength of final product^[6]. In our previous study, it has been found that 20 wt% PEO E-30 hydrogel film has better mechanical properties as

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wound dressing^[7]. In order to further improve the mechanical properties of the PEO hydrogel films, in the present work, PEO graft hydrogel films by EB irradiation of PEO E-30 or R-150 aqueous solutions incorporated with PVA at different ratio were prepared. Physiochemical properties of the PEO graft hydrogel films such as gel fraction, degree of swelling, tensile strength and elongation at break were investigated as a function of production factors combination e.g. radiation dose, concentration and ratio of the polymers.

2 EXPERIMENTAL

2.1 Materials

PEO E-30 and R-150 were supplied by Ichimaru Pharcos Co. Ltd., Japan. Their molecular weights were $(3 \sim 5) \times 10^5$ and $(1 \sim 1.7) \times 10^5$ respectively. PVA was produced by Kuraray Co. Ltd. Japan. Methanol is analytical reagent, and water in this experiment is distilled water.

2.2 Preparation and measurement of the PEO graft hydrogel films

The concentration of the blends of PEO E-30 or R-150 with PVA investigated was 10 wt% and 20 wt%. The ratio of PEO with PVA in the 10 wt% blends was 4:1 and 3:2, and that of both polymers in the 20 wt% blends was 9:1, 4:1 and 7:3. The PVA concentration investigated was 20 wt% as a contrast. The levels of EB irradiation dose were 20, 40, 60, 80 and 100 kGy. To obtain the aqueous solutions of the polymers, the polymers were added to distilled water, then stirred and heated to 121°C for 120 min in an autoclave. After obtaining completely homogeneous solutions they were poured into Petri dishes at room temperature (25°C). The sample solutions was 2 mm thickness. To yield crosslinking hydrogel films, the polymer solutions were irradiated using electron beams at current of 2 mA and an acceleration energy of 0.8 MeV generated from a Cockroft Walton Electron Beam Accelerator at a dose rate of 20 kGy/pass and a temperature of 25 °C under forced cooling with a fan. Then the chemical and mechanical properties of the PEO graft hydrogel films such as gel fraction, degree of swelling, tensile strength and elongation at break were measured according to the methods previously reported by Yang *et al*^[7].

3 RESULTS AND DISCUSSION

3.1 Radiation crosslinking of PEO R-150 and E-30 graft hydrogel films

Gel fraction of the PEO R-150 and E-30 graft hydrogel films formed by EB irradiation of PEO R-150 or E-30 aqueous solutions incorporated with PVA at different ratio was given in Fig.1 and Fig.2. It can be seen from Fig.1 that the gel fraction of the PEO R-150 graft hydrogel films increased obviously with the increase of irradiation dose, while it decreased when concentration of PEO R-150 blend increased from 10 wt% to 20 wt%. It can be seen from Fig.2 that the gel fraction of the PEO E-30 graft hydrogel films mainly depended on irradiation dose. The degree of crosslinking of the PEO E-30 and R-150 graft hydrogel films increased slightly with the increase of PVA content, but their gel fraction was lower than that of pure PVA hydrogel film of 20 wt%.

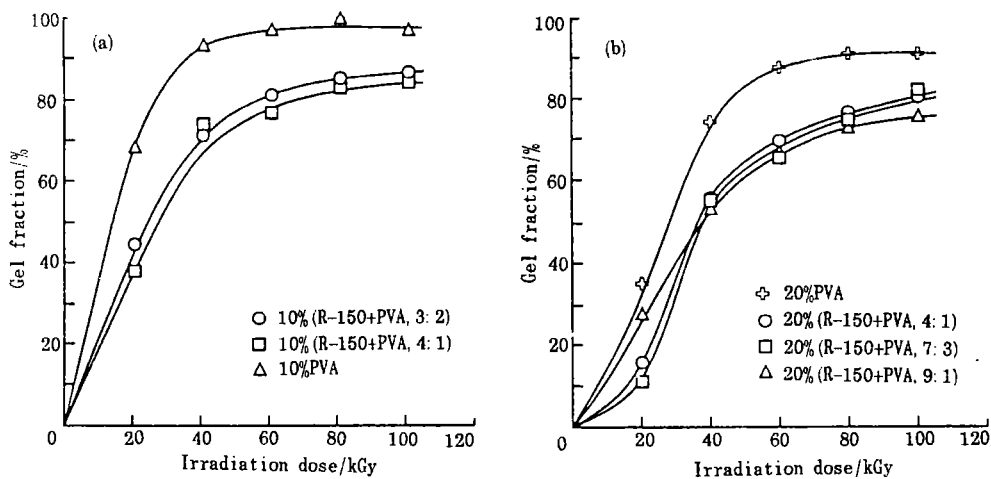


Fig.1 Gel fraction of the hydrogel films obtained by EB irradiation of aqueous solutions of blended PEO R-150/PVA

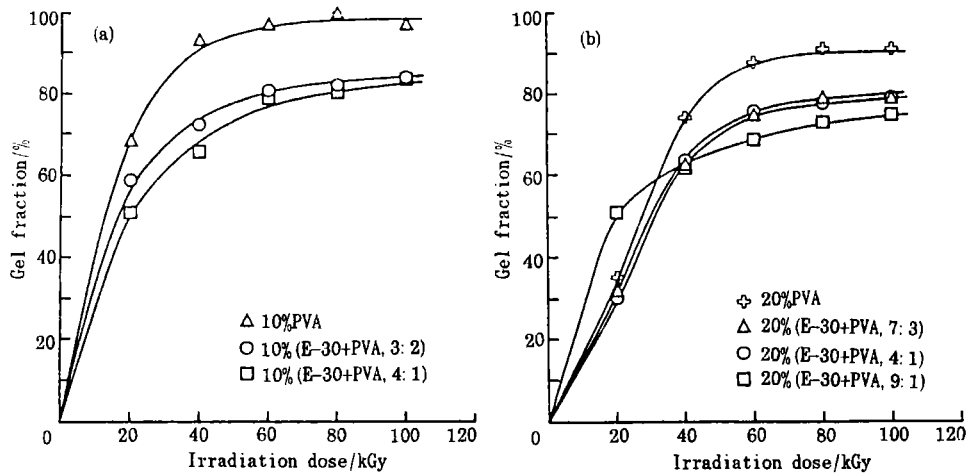


Fig.2 Gel fraction of the hydrogel films obtained by EB irradiation of aqueous solutions of blended PEO E-30/PVA

3.2 Swelling properties of both the PEO graft hydrogel films

The degree of swelling of both the PEO graft hydrogel films obtained by EB radiation of the aqueous solutions of the blends of PEO with PVA was shown in Fig.3 and Fig.4. It was seen that the degree of swelling of the PEO graft hydrogel films decreased obviously with the increase of PVA content, while these degrees of swelling were higher than that of pure PVA hydrogel films. Effect of irradiation dose, polymer concentration and molecular weights on the degree of swelling of the PEO graft hydrogel films was similar to the pure PEO hydrogel films. The water content of hydrogels can be varied over a wide range with the radiation dose and the polymer concentration^[8]. It is interesting to note that the degree of swelling of the PEO E-30 graft hydrogel film of 20 wt% (E-30+PVA, 7:3) is the lowest, while its gel fraction is the highest in the three PEO graft hydrogel films. The results

indicate that the equilibrium water content of the gels depends on several parameters, among which are the crosslink density and the nature and number of the hydrophilic sites in the macromolecular matrix^[4]. The PVA can reduce the degree of swelling of the PEO graft hydrogel films, thus increasing the mechanical strength of the PEO graft hydrogel films^[6].

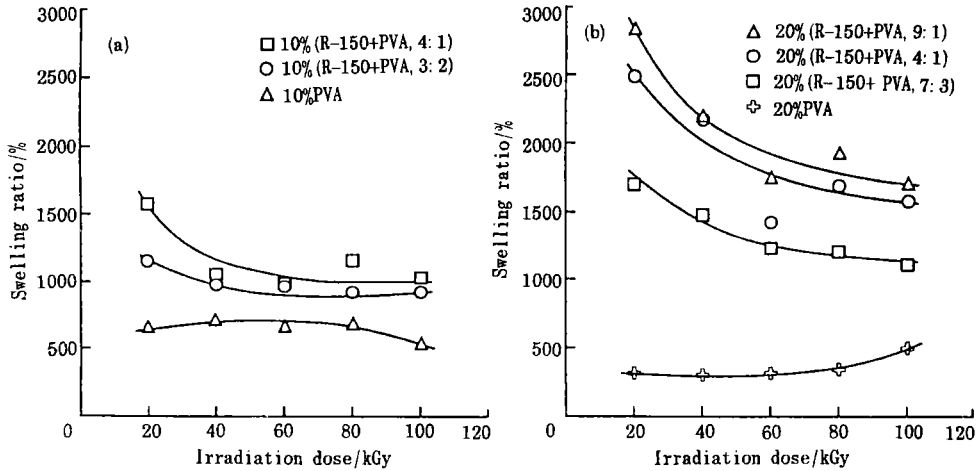


Fig.3 Swelling ratio of hydrogels obtained by EB irradiation of blended PEO R-150/PVA aqueous solutions at different ratio

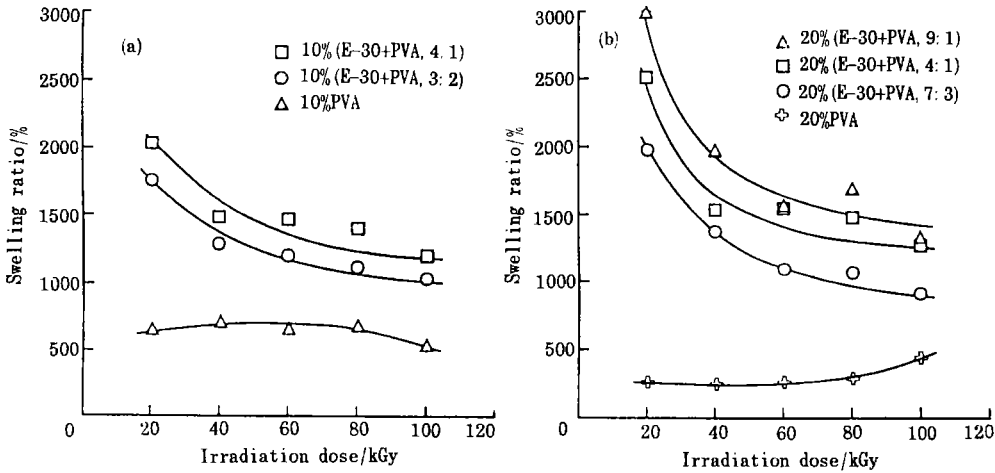


Fig.4 Swelling ratio of the hydrogel film obtained by EB irradiation of aqueous solutions of blended PEO E-30/PVA at different ratio

3.3 Tensile strength of the PEO E-30 graft hydrogel films

The PVA hydrogel films obtained by EB irradiation of its aqueous solutions possessed better physical properties e.g. transparency and fews of bubbles, but it was poorer and fragile in mechanical strength, so its tensile strength and elongation at break could not be measured. However, it can be seen from Fig.5 that with the increase of PVA content in the blend solutions, the tensile strength of the PEO graft E-30 hydrogel films of 20 wt% increased obviously, thus the mechanical strength of the

PEO E-30 graft hydrogel film of 20 wt% at ratio of 7:3 was the highest in the three PEO E-30 hydrogel films. The mechanical strength of the graft hydrogel film of 20 wt% (E-30+PVA,9:1) was higher than that of 20 wt% (E-30+PVA, 4:1). It may be related to the influence of PEO E-30 concentration on the tensile strength. As has been demonstrated in previous study^[7], the tensile strength of PEO E-30 hydrogel films increased dramatically with the increase of the polymer concentration. Thus, it was not obvious for the increasing effect of PVA on the tensile strength of the PEO E-30 hydrogel films under both the ratio of PVA incorporation. It also can be seen that with the increase of the irradiation dose, the tensile strength of the PEO E-30 graft hydrogel film of 20wt% at a ratio of 7:3 decreased slowly, but it was obviously higher than that of the pure PEO E-30 hydrogel film of 20 wt%, when compared with our previous study^[7]. The results indicated that PVA has an increasing effect on the mechanical strength of the PEO E-30 graft hydrogel film of 20wt%. Maybe it is due to PVA incorporated reduced the degree of swelling of the PEO E-30 graft hydrogel films thus increasing their tensile strength. The tensile strength and elongation at break of the PEO R-150 graft hydrogel films of 20wt% at any ratio was too weak to be measured. These results show that the PEO E-30 graft hydrogel film of 20wt% at ratio of 7:3 is a very ideal biomedical material as a wound dressing, especially at irradiation dose of 40kGy.

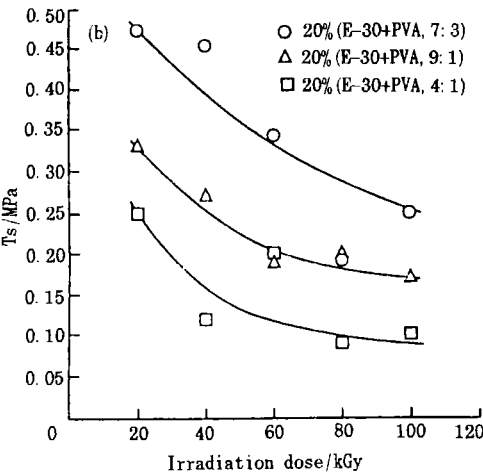


Fig.5 Tensile strength of the hydrogel films obtained by EB irradiation of aqueous solutions of blended PEO E-30/PVA at different ratio

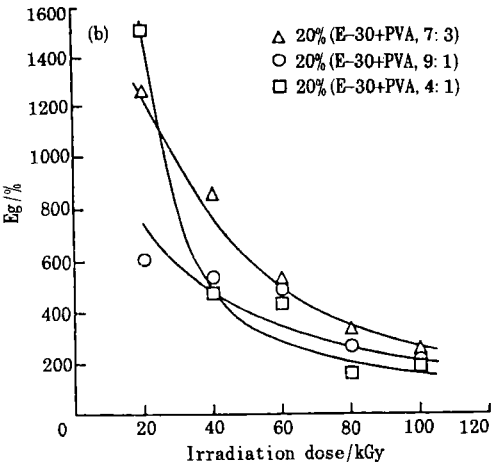


Fig.6 Elongation of the hydrogel films obtained by EB irradiation of aqueous solutions of blended PEO E-30/PVA at different ratio

3.4 Elongation at break of the PEO E-30 graft hydrogel films

The elongation at break of the PEO E-30 graft hydrogel films was shown in Fig.6. It was seen that the increase of the irradiation dose produced a negative effect on the elongation at break. Although the elongation at break of the PEO E-30 graft hydrogel film at a ratio of 7:3 was lower, it was enough as a wound dressing.

4 CONCLUSIONS

This paper reported the influences of the experimental factors (radiation dose, concentration and blending ratio of polymers) on the measured chemical and mechanical properties (gel fraction, degree

of swelling, tensile strength and elongation at break) of the PEO hydrogel films grafted PVA. The radiation dose increase has a positive effect on the degree of crosslinking, and a negative effect on the degree of swelling, the tensile strength and elongation at break of the PEO graft hydrogel films. The polymer concentration increase has a negative effect on the degree of crosslinking and a positive effect on the degree of swelling. The increase of ratio of PVA incorporated has a positive effect on the gel fraction and the tensile strength and a negative effect on the degree of swelling. PVA can improve the mechanical strength of the PEO E-30 hydrogel films through reducing the degree of swelling of the PEO E-30 hydrogel films after radiation graft. The results indicate that the PEO E-30 graft hydrogel film of 20wt% at a ratio of 7:3 possesses better physiochemical properties such as more moderate gel fraction, swelling ratio and elongation at break, especially its higher tensile strength at irradiation dose of 40kGy as a wound dressing.

References

- 1 Peppas N A, Scott J E. *J Controlled Release*, 1992, 18:95~100
- 2 Yates D W, Hadfield J M. *Injury*, 1984, 16:230~232
- 3 Yoshii F, Makuuchi K, Darwis D *et al.* *Radiat Phys Chem*, 1995, 46:169~174
- 4 Sederel L C, Van der Does L, Euverman B J *et al.* *Biomaterials*, 1983, 4:3~8
- 5 Corkhill P H, Hamilton C J, Tighe B J. *Biomaterials*, 1989, 10:3~10
- 6 Anseth K S, Bowman C N, Brannon-Peppas L. *Biomaterials*, 1996, 17:1647~1657
- 7 YANG Z S, Yoshii F, Makuuchi K. *Radiat Res Radiat proces (in Chinese)*, 1998, 16(4):198~203
- 8 Ikada Y, Mita T, Horii F *et al.* *Radiat Phys Chem*, 1977, 9:633~645

聚氧化乙烯水凝胶膜的辐射接枝研究

杨占山

(苏州医学院放射医学系 苏州 215007)

吉井文男 幕内惠三

日本原子能研究所高崎辐射化学研究所

摘要 为了得到一种理想的水凝胶伤口敷料, 研究了应用电子束辐射接枝了不同比例聚乙烯醇 (PVA) 的聚氧化乙烯 (PEO) 水凝胶膜的制备和该膜的理化特性。实验结果显示, PEO 接枝水凝胶膜的凝胶分数主要依赖于辐射剂量和聚合物浓度。而其溶胀度与辐射剂量聚合物的浓度, 混合比例和分子量密切相关。该膜的抗张强度和断裂伸长率则明显地依赖于辐射剂量和聚合物的混合比例。实验发现, 比例为 7:3 的 20wt% PEO E-30 接枝水凝胶膜与其它 PEO 接枝水凝胶膜和单纯 PEO E-30 水凝胶膜相比具有较好的理化特性, 例如韧性, 较少气泡, 适度的凝胶分数, 溶胀度和断裂伸长率, 尤其它的较高的抗张强度。实验结果表明, PVA 在辐射接枝后能够通过降低 PEO 水凝胶膜的溶胀度而改善 PEO 水凝胶膜的机械强度。

关键词 聚氧化乙烯, 聚乙烯醇, 水凝胶, 特性, 辐射接枝