

ASSESSMENT OF PROPERTIES OF HYDROGEL FILMS FORMED BY IRRADIATION OF POLY (ETHYLENE OXIDE)

Yang Zhanshan⁽¹⁾ Fumio Yoshii⁽²⁾ Keizo Makuuchi⁽²⁾

⁽¹⁾(Suzhou Medical College, Suzhou 215007)

⁽²⁾(Takasaki Radiation Chemistry Research Establishment, Japan Atomic Energy Research Institute,
Takasaki, Japan)

ABSTRACT Poly(ethylene oxide)(PEO) hydrogel films formed by electron beam (EB) irradiation were prepared as wound dressing. The physiochemical properties of the PEO hydrogel films were evaluated. The results showed that properties of the PEO hydrogel films were largely dependent on irradiation dose, polymer concentration and its molecular weight. As the EB irradiation dose increased, the gel fraction and the hardness of the PEO hydrogel films also increased, while its degree of swelling, the tensile strength and elongation at break decreased dramatically. With the increase of the polymer concentration, the degree of swelling, the tensile strength and elongation at break of the PEO E-30 hydrogel films increased significantly, while their gel fraction and hardness decreased obviously. When the PEO molecular weight increased, the gel fraction, the degree of swelling and the hardness of the PEO hydrogel films increased obviously as well. The experimental results indicated that the PEO E-30 hydrogel film of 20 wt% possessed a better mechanical strength than other PEO hydrogel films, especially at doses of 40~60 kGy.

KEYWORDS Poly(ethylene oxide), Hydrogel, Radiation, Crosslinking, Mechanical strength

A hydrogel is defined as a slightly or moderately crosslinked polymer which has the ability to swell but not to dissolve and retain a significant fraction of water in its structure^[1]. Hydrogels are very useful as biomedical materials. they usually show good biocompatibility, high oxygen and water vapour permeability and controlled drugs release etc. Hydrogels are widely applied as wound dressings, artificial skin and drug delivery systems etc. The hydrogel films of PEO, poly (vinyl alcohol) (PVA) and poly (vinyl pyrrolidone) (PVP) have been applied to no-adhesive membrane for intestine and heart, and all kinds of skin damages such as burns, bedsores and scalds etc^[2~4]. However, the mechanical strength of the radiation-crosslinked hydrogel films was not high enough for biomedical applications. In order to get a more ideal wound dressing, in the present study the influence of production factors e.g. irradiation dose, polymer concentration and molecular weight on physiochemical properties of PEO hydrogel films such as gel fraction, degree of swelling, hardness, tensile strength and elongation at break was investigated.

1 Experimental

1.1 Materials

All the materials used in this study were commercially available; PEO was supplied by Ichimaru Pharcos Co. Ltd., Japan. Three types of PEO were used in this experiment. The molecular weights of PEO R-150, PEO E-30 and PEO E-160 are $(1\sim1.7)\times10^5$, $(3\sim5)\times10^5$ and $(3.6\sim4)\times10^6$ respectively. Methanol was analytical grade reagent, and water in this experiment is distilled water.

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1.2 Preparation of PEO hydrogel films

Given concentrated aqueous solutions of PEO were prepared using an autoclave at 121°C for 120 min. The sample concentration (w/w) investigated was 5%, 10%, 15% and 20%. The homogeneous solutions were poured into Petri dishes at room temperature. The thickness of solutions was 2 mm. Then the 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 dose rate of 20 kGy/pass under forced cooling with a fan (Maximum acceleration energy and current are 2 MeV and 30 mA respectively) to yield crosslinked hydrogels. After irradiation, chemical and physical properties such as gel fraction, degree of swelling, hardness, tensile strength and elongation at break of the hydrogels were measured.

1.3 Gel fraction

The dried hydrogel samples were put into stainless meshes. The sol was extracted in water at 121°C for 2 hours by using an autoclave. Then the gel was put into the methanol solution for 1 hour and dried in a vacuum oven at 50°C for 24 hours. The gel fraction was defined as the ratio of the weight of the dried gel to the initial weight of polymer.

$$\text{Gel} = (\text{weight of dried gel} / \text{weight of initial polymer}) \times 100\%$$

1.4 Degree of swelling

The degree of swelling in water is defined as the ratio of the weight of water in a swollen gel to the weight of the dried hydrogel. The swollen gel was measured by allowing hydrogel samples to equilibrium state in distilled water at the room temperature (25°C). The dried hydrogel weight was determined by drying the hydrogel samples to constant weight in a vacuum oven at 50°C.

1.5 Hardness

Hardness of the irradiated hydrogel films were measured by Nichiban Co. Ltd. Japan using a hardness tester MD-1.

1.6 Tensile strength and elongation at break

The irradiated hydrogel samples were cut into dumbbell shapes according to ASTM D-1822-L model. Then the physical properties of the samples such as tensile strength and elongation at break were measured using a Stograph-R1 tension meter (Toyo Seiki Co. Ltd., Japan) with a crosshead speed of 150 mm/min and load selector of $\times 50$. The thickness of samples were measured using a thickness tester (Mitutoyo, Japan).

2 Results and discussion

2.1 Degree of crosslinking of the PEO hydrogel films

As is well-known, a hydrogel is a slightly or moderately crosslinked polymer. The extent and homogeneity of crosslinking are greatly dependent on the molecular state of the polymer chains, and intimately related to irradiation dose and polymer concentration^[5]. Gel fraction of the PEO hydrogel films obtained by EB irradiation of PEO E-30, R-150 and E-160 solutions was shown in Fig. 1 and Fig. 2. It can be seen from Fig. 1 that the gel fraction increased rapidly when irradiation dose increased from 0 to 40 kGy, then the amounts of gel slowly increased until saturation. The result was consistent with a previous study about the effect of radiation on PVA solution^[5]. Higher the PEO E-30 concentration was, smaller the gel fraction of PEO E-30 was, at above a dose of 40 kGy. It can be seen from Fig. 2 that gel fraction of the PEO hydrogel films of bigger molecular weight was obviously higher than that of smaller molecular weight at the same dose. The recent research also showed the effect of the PEO

molecular weight on the cross-link density^[6].

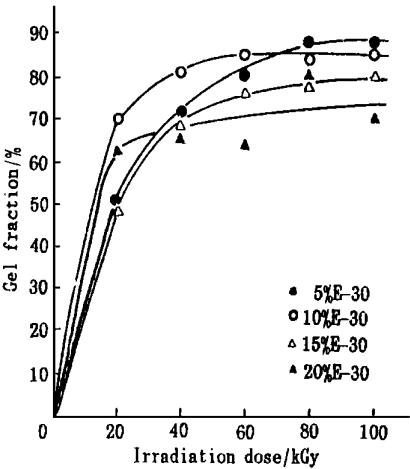


Fig. 1 Gel fraction of the hydrogel films obtained by EB irradiation of PEO E-30 aqueous solutions of different concentration

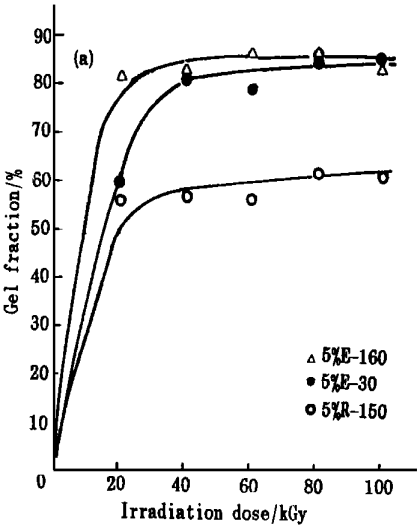


Fig. 2 Comparison of gel fraction of the hydrogel obtained by EB irradiation of PEO aqueous solutions of different molecular weight

2.2 Swelling behaviour of PEO hydrogel films

The degree of swelling is intimately related to the material strength and absorbency of a hydrogel^[7]. The degree of swelling of the PEO hydrogel films obtained by EB irradiation of its aqueous solutions was shown in Fig. 3 and 4. The results showed that the degree of swelling of the PEO E-30 hydrogel films decreased significantly with the increase of the irradiation dose, but it increased with the increase of the polymer concentration. Water content of hydrogels can be varied over a wide range with the radiation dose and the polymer concentration. The swelling ratio of the PEO hydrogel film of bigger molecularweight was slightly higher than that of smaller molecular weight at 5% PEO solution. However, the effect of different

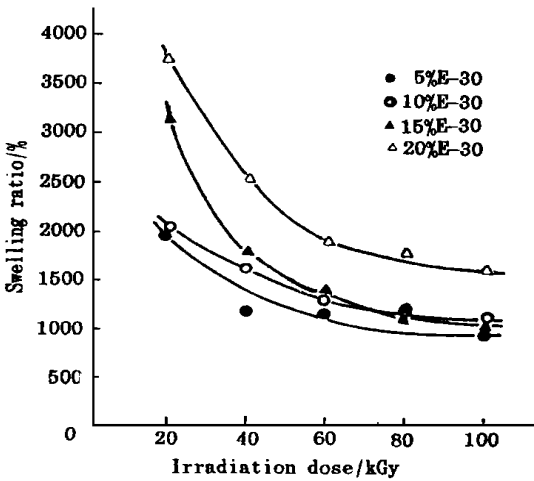


Fig. 3 Swelling ratio of the hydrogel films obtained by EB irradiation of PEO E-30 aqueous solutions of different concentration

refuted our expectation at 15% PEO solution.

2.3 Effect of experimental factors on hardness of the PEO hydrogel films

Hardness of the PEO hydrogel films of different molecular weight or concentration was shown in Fig. 5 and 6. The results showed that as irradiation dose increased, the hardness of the PEO hydrogel films increased dramatically as well. However, as the polymer concentration increased, the hardness of the PEO hydrogel films decreased obviously. The hardness of the PEO E-30 hydrogel films of bigger molecular weight was obviously higher than that of the PEO R-150 hydrogel films of smaller molecular weight.

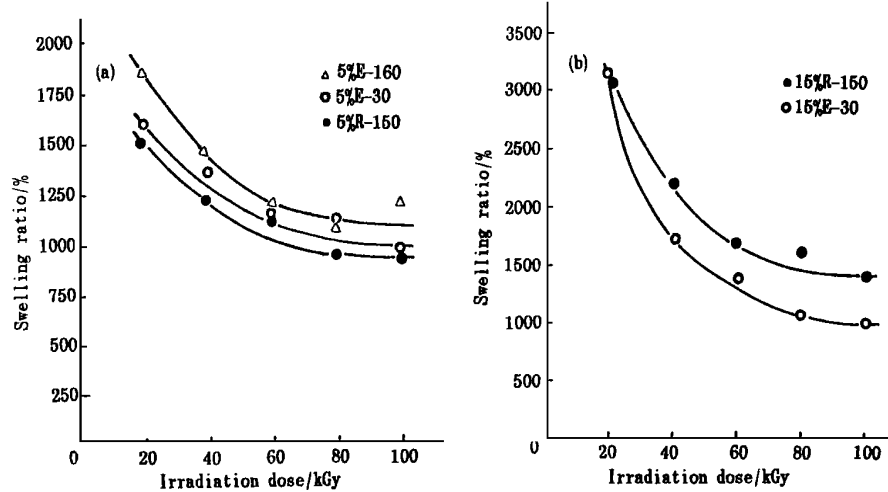


Fig. 4 Comparison of swelling ratio of the hydrogel films obtained by EB irradiation of PEO aqueous of solutions of different molecular weight

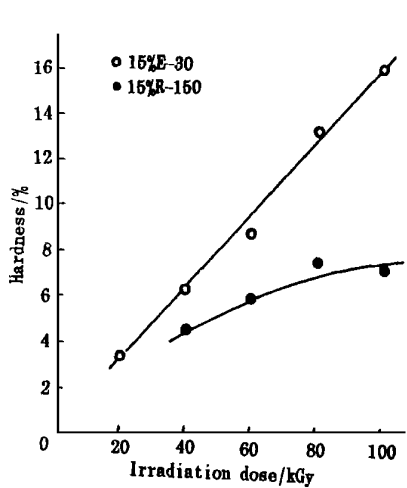


Fig. 5 Hardness of the hydrogel films obtained by EB irradiation of aqueous solutions of PEO R-150 and E-30

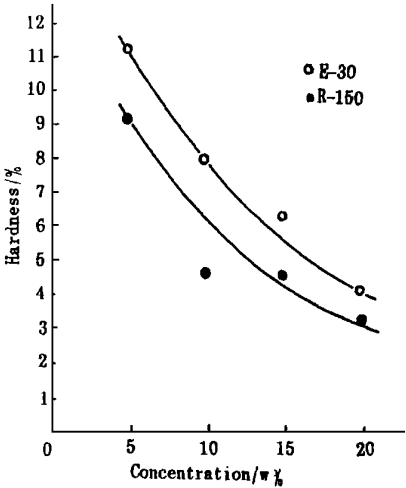


Fig. 6 Hardness of the hydrogel films obtained by EB irradiation of aqueous solutions of PEO R-150 and E-30 at dose of 40 kGy

2.4 Tensile strength and elongation at break of the PEO hydrogel films

The PEO E-30 hydrogel films obtained by EB irradiation of its aqueous solutions possesses better mechanical properties. Its tensile strength and elongation at break were given in Fig. 7~10. It can be seen from Fig. 7 that with the increase of the irradiation dose the tensile strength of the 20% PEO E-30 hydrogel film decreased significantly, while that of the 15% PEO E-30 hydrogel film increased gradually. The result from Fig. 8 showed an obvious increase of the tensile strength of the PEO E-30 hydrogel film with the increase of the polymer concentration. The results from Fig. 9 and 10 showed that the elongation at break of the PEO E-30 hydrogel films decreased obviously with the increase of irradiation dose, but it increased strongly with the polymer concentration. The PEO hydrogel films of

(5~20)% R-150 and (5~10)% E-30 obtained by EB irradiation of their aqueous solutions were poorer and fragile in mechanical strength. It is impossible for us to prepare PEO E-160 solutions of 6% and over due to its higher molecular weight. Hence the tensile strength and elongation at break of PEO R-150 and E-160 can not be measured. The data indicated that the mechanical strength of the PEO hydrogel films is mainly dependent on irradiation dose, polymer concentration and molecular weight of polymer^[1]. It is found from Fig. 7 that the 20% PEO E-30 hydrogel film has a better mechanical strength than the 15% PEO E-30 hydrogel film, especially at dose of 40~60 kGy.

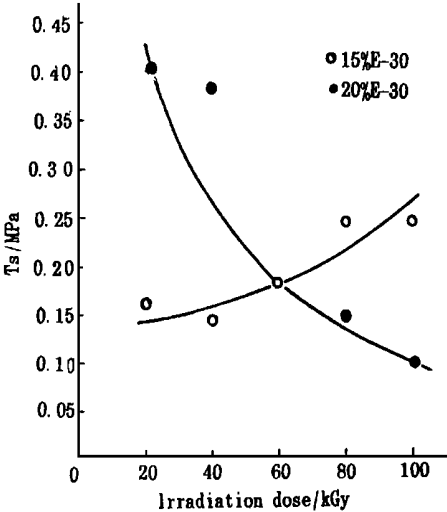


Fig. 7 Tensile strength of the hydrogel films obtained by EB irradiation of PEO E-30 aqueous solutions

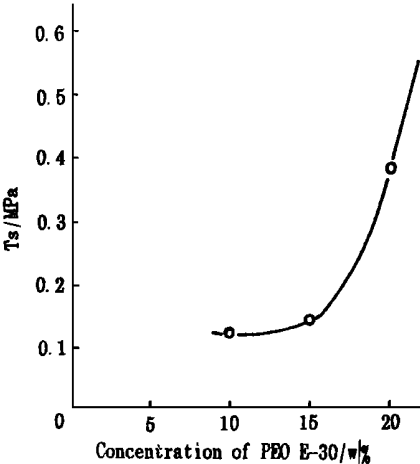


Fig. 8 Tensile strength of the hydrogel films obtained by EB irradiation of PEO E-30 aqueous solutions at dose of 40 kGy

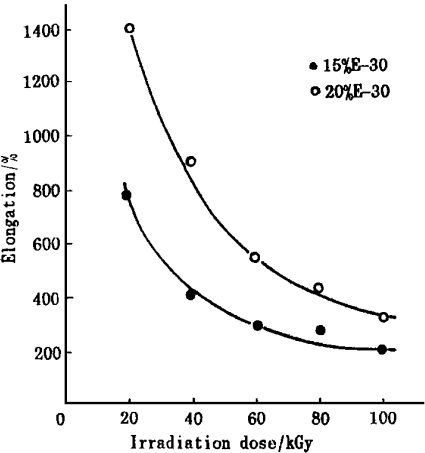


Fig. 9 Elongation of the hydrogel films obtained by EB irradiation of PEO E-30 aqueous solutions with different concentration

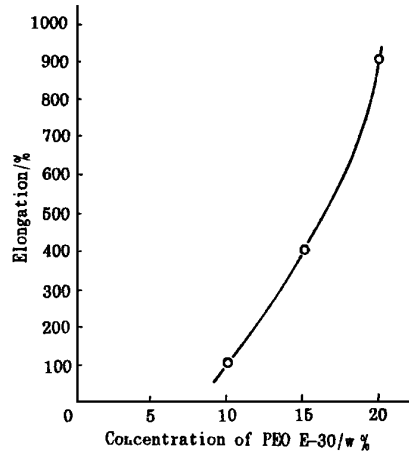


Fig. 10 Elongation of the hydrogel films obtained by EB irradiation of PEO E-30 aqueous solutions at dose of 40 kGy

3 Conclusions

The crosslinking behaviour and physical properties of PEO R-150, E-30 and E-160 hydrogel films have been studied. The results showed that gel fraction of the PEO hydrogel films increased with the increase of EB irradiation dose and molecular weight, while it decreased with the increase of the PEO E-30 concentration. Degree of swelling of the PEO hydrogel films decreased with the increase of irradiation dose, while it increased with the increase of the PEO E-30 concentration and PEO molecular weight of 5% except 15% PEO. Hardness of the PEO hydrogel films increased dramatically with the increase of irradiation dose and PEO molecular weight, while it decreased with the increase of the polymer concentration. Tensile strength and elongation at break of the PEO E-30 hydrogel films decreased significantly with the increase of irradiation dose, while it increased with the increase of the polymer concentration. It was found that 20% PEO E-30 hydrogel film had a better mechanical strength than other PEO hydrogel films, especially at the irradiation doses of 40~60 kGy.

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辐照聚氧化乙烯形成的水凝胶膜的性能评价

杨占山 吉井文男⁽¹⁾ 幕内惠三⁽¹⁾

(苏州医学院放射医学系 苏州 215007)

⁽¹⁾(日本原子能研究所高崎辐射化学研究所)

摘要 研究应用电子束照射聚氧化乙烯(PEO)所形成的水凝胶膜的制备,并对这些可作为伤口敷料的水凝胶膜的理化特性进行了评价。结果显示,PEO水凝胶膜的特性极大地依赖于辐射剂量、聚合物浓度及其分子量。随着辐射剂量的增加,PEO水凝胶膜的凝胶分数和硬度明显增加,而其膨胀度、抗张强度和断裂伸长率明显减低。聚合物浓度的增加能引起PEO E-30水凝胶膜的膨胀度、抗张强度和断裂伸长率明显增加,而其凝胶分数和硬度明显减低。当PEO分子量增加时,其水凝胶膜的凝胶分数、膨胀度和硬度亦明显增加。结果表明,40~60kGy照射的20% PEO E-30水凝胶膜具有较理想的机械强度。

关键词 聚氧化乙烯,水凝胶,辐射,交联,机械强度