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Radiation Physics and Chemistry 55 (1999) 709–712

Radiation Physics and Chemistry

www.elsevier.com/locate/radphyschem

Crosslinking and degradation of PVP hydrogels as a function of dose and PVP concentration

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Abstract

Swelling was performed on dried membranes, normal ones and dried gel to unravel the role of crosslinking and degradation on polymeric structure during drying and hydration process. The comparison of the swelling results suggested that the network were formed only by PVP molecules. The complex mixture of macromolecules showed a irreversible behavior upon drying and hydration, probably as a function of PEG and/or agar entangling in effective physical crosslink. The best network regularity and useful properties was found at 20–30 kGy. © 1999 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Crosslinking and degradation of PVP hydrogels

1. Introduction

Hydrogels based on poly(vinylpyrrolidone) (PVP) produced by radiation-induced crosslinking and simultaneous sterilization has been applied successfully as local dressings on wound treatments, such as burns, skin's ulceration and postoperative dressings. The production process of these hydrogels based on the method developed by Rosiak et al. (1989, 1995) has been transferred to IPEN laboratories as part of an IAEA program. Now IPEN has undertaken efforts for its transference to the Brazilian society by the combined action of its laboratories, industry and hospitals. One of the most important therapeutic characteristics of these membranes is its capacity to absorb body fluids, which is directly related to the crosslinking density of the network formed during the irradiation (Zang et al., 1985). Another important characteristic is its fast drying rate over the skin (Lugao et al., 1998). The positive side of the drying process is the increase in the capacity of water absorption and the temperature control of the wound. The negative one is the necessity of dressing replacement at least twice a day. Some clinical procedures are feasible to avoid dryness as wetting the membrane from time to time. This study addresses the structural changes during hydration and drying of membranes with various PVP concentration and irradiation doses by studying the swelling behavior of the hydrated membrane, the dried one and the extracted gel after drying.

2. Materials and methods

All the materials used in this study were medical grade: poly(vinylpyrrolidone)/PVP-K90 of PLASDONE; agar/Agar Technical No. 3 of OXOID; poly(ethylene glycol)/ATPEG-300 of OXITENO. The membranes were prepared with PVP concentration of 2, 5, 8, 10, 12 and 16%. PEG and agar concentrations were maintained at 3 and 0.8%, respectively. The 3 mm

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PII: S0969-806X(99)00216-9

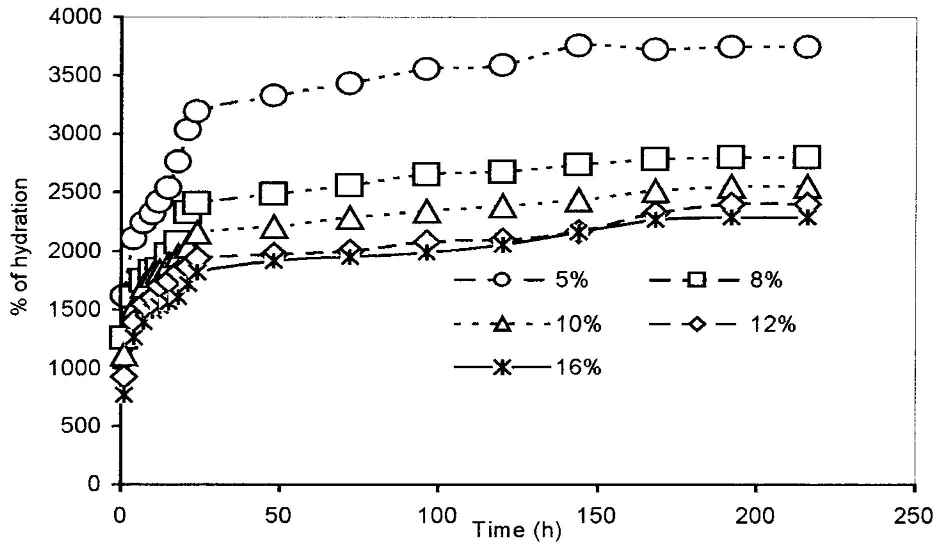

Fig. 1. Swelling as a function of time and PVP concentration.

thickness membranes were obtained by pouring the hot solution in moulds, which, after cooling, were packed and irradiated at room temperature.

2.1. Gel fraction

The samples were washed in sohxlet extractors with boiling water for 36 h. The obtained gels were dried until constant weight.

2.2. Hydration

The samples were maintained in water for a period of 216 h. The water absorption was checked every hour in the first 24 h run and, after that, each measurement was performed 24 h later until constant weight was obtained. The hydration grade was determined by the difference of the weight after and before hydration.

3. Results and discussion

The swelling behavior of the hydrated membranes (corrected for the dry mass) as a function of time of hydration and PVP concentration was shown in Fig. 1; and the dose effect on swelling was shown in Fig. 2. Fig. 1 shows the usual shape for the swelling of hydrogels. Three different kinetics were observed. The first stage at the very beginning, a very fast absorption due to surface hydrophilicity and capillarity was observed. The second stage ended with about 24 h and the stepwise slowdown of the absorption to almost constant values typical of diffusion mechanism was possible to recognize. In the last step, a minor increase in water content based on a very slow network relaxation was detected.

The decrease in water uptake with dose for PVP concentration from 5 to 16% was shown in Fig. 2. There were two stages of water absorption. A faster decrease linked with the increase in crosslinking den-

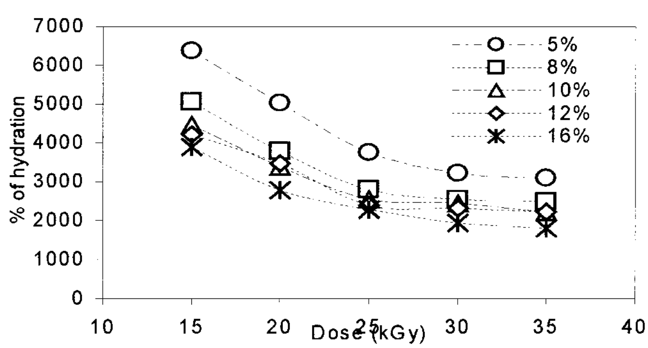

Fig. 2. Equilibrium swelling based on dry mass (256 h) as a function of [PVP] and dose.

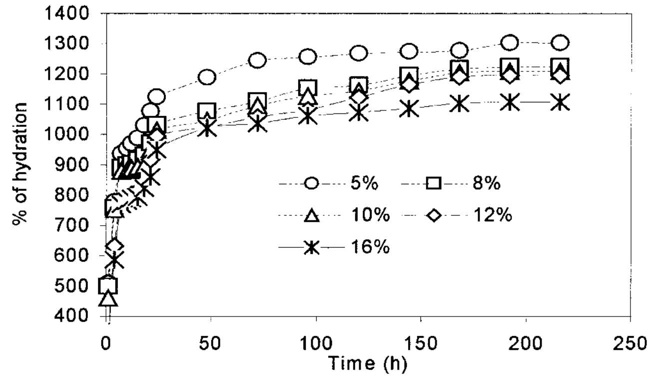

Fig. 3. Swelling of the dried membrane as a function of time and [PVP] (dose of 25 kGy).

sity with consequent decrease in network mobility followed by a slowdown caused by the already high level of structural rigidity.

Swelling of the dried membranes was studied for the purpose of evaluation of the degradation process during drying and swelling, as shown in Figs. 3 and 6. Fig. 3 showed exactly the same pattern as Fig. 1. However, the equilibrium values were much lower, indicating an increasing degree of crosslinking density upon the drying process. This behavior could be explained by the formation of high concentration of entanglements. Only a small decrease in swelling capacity with dose and PVP concentration was observed when compared with those obtained for the hydrated membrane. This behavior of the dried membrane showed a small dependence on the original crosslinking density created by recombination of PVP macroradicals after irradiation. The drying process created another structural fixture by connecting or entangling the molecules and hindering the swelling of the network.

The abnormal behavior of the swelling of the dried membrane was compared with the swelling of the dried gel fraction (Figs. 5 and 6.); as the gel was supposed to be composed solely by covalent crosslinked PVP molecules. Fig. 5 is similar to Fig. 3 at all doses and swelling time, even being the dried gel subjected to 36 h of boiling water followed by the drying process. The first immediate conclusion was that there were no degradation taking place during the boiling and drying process. The PVP network was extremely resistant to degradation even after some hydrolization as a result of the irradiation process. The second conclusion is that there were no new physical crosslinking taking place as the swelling values reach closely to the same order of magnitude of the original membrane.

4. Conclusion

The process of drying a complex mixture of macromolecules like PVP, PEG and agar showed an irreversible behavior upon hydration, probably as a function of physical crosslinking. The comparison of the swelling results suggested that the network was formed only by PVP molecules. Nevertheless, PEG or agar were able to entangle in very effective physical crosslink. The membranes produced with 5% PVP showed

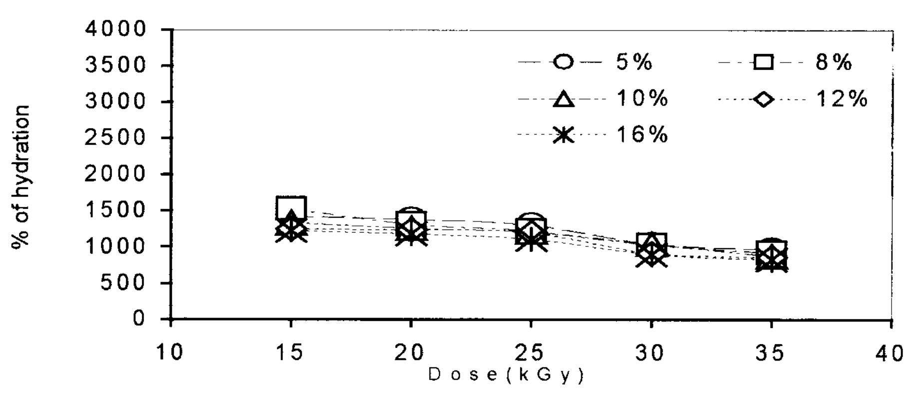

Fig. 4. Equilibrium swelling (256 h) of the dried membrane as a function of [PVP] and dose.

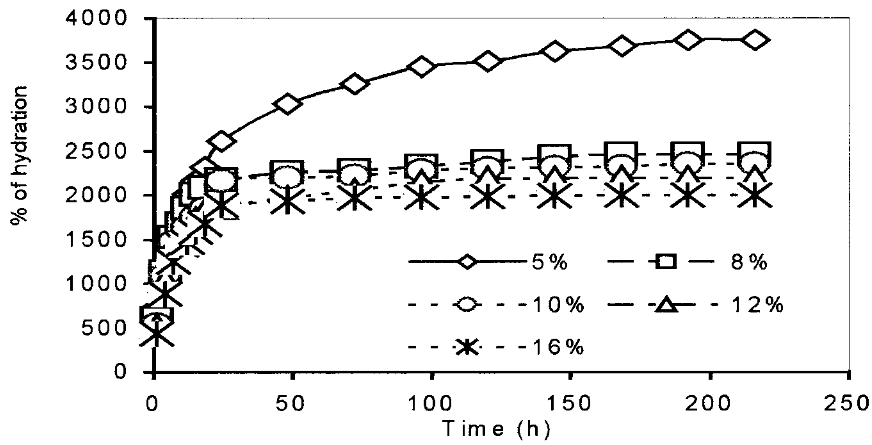

Fig. 5. Swelling of the dried gel as a function of time and PVP concentration (dose of 25 kGy).

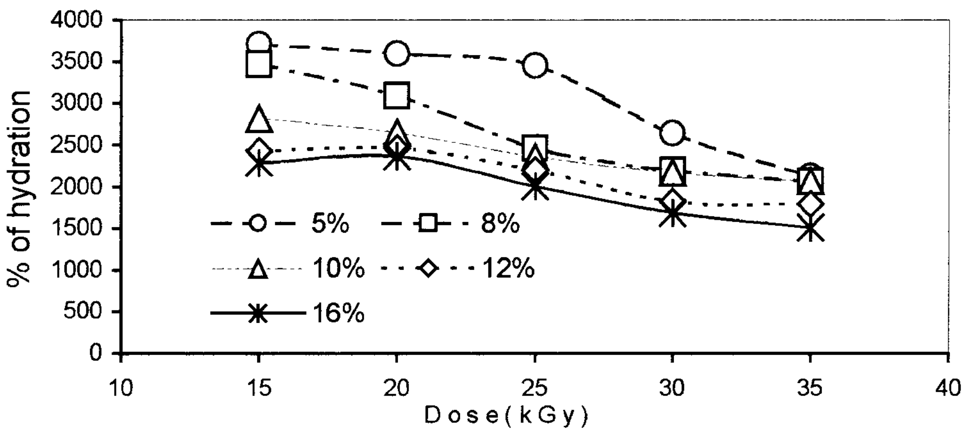

Fig. 6. Equilibrium swelling (256 h) for the dried gel as a function of PVP concentration and dose.

a very high swelling level if compared with membranes produced with 8% and over for almost all studied doses. This suggested the existence of some critical concentration of PVP at each molecular weight level; under this level the formation of a regular mesh was more difficult as the molecules were far apart. The range of dose of 20–30 kGy showed the best results regarding network regularity and useful properties.

Acknowledgements

The authors would like to thank J.M. Rosiak, E.S.R. Somessari and C.G. da Silveira for their contribution for this work. The support given by the IAEA is gratefully acknowledged.

References

Lugao, A.B., Machado, L.D.B., Miranda, L.F., Alvarez, M.R., Rosiak, J.M., 1998. Study of wound dressing structure and hydrating/dehydrating properties. Radiat. Phys. Chem. 56 (16), 319.

Rosiak, J.M., Rucinska-Rybus, A., Pekala, W., 1989. Method of manufacturing of the hydrogel dressings. U.S. Patent No. 4,871,490.

Rosiak, J.M., Ulanski, P., Pajensky, L.A., Yoshii, F., Makuuchi, K., 1995. Radiation formation of hydrogels for biomedical purpose. Some remarks and comments. Radiat. Phys. Chem. 46 (2), 161.

Zang, W., Sun, J., Quian, B., 1985. Structure effects on the sol fraction-dose relationship in radiation crosslinking of polymers. Polymer Communication 59 (1), 17.