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Water diffusion into radiation crosslinked PVA–PVP network hydrogels

David J.T. Hill [a,*], Andrew K. Whittaker [b,c], Zainuddin [b,d,e]

[a] School of Chemistry and Molecular Biosciences, The University of Queensland, Brisbane, 4072, Australia
[b] Australian Institute of Bioengineering and Nanotechnology, The University of Queensland, Brisbane, 4072, Australia
[c] The University of Queensland, Centre for Advanced Imaging, St Lucia, Brisbane, 4072, Australia
[d] Queensland Eye Institute, Brisbane, 4101, Australia
[e] School of Medicine, The University of Queensland, Brisbane, 4006, Australia

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ABSTRACT

A series of hydrogels comprised of crosslinked networks of poly(vinyl alcohol), PVA and poly(vinyl pyrrolidone), PVP, have been prepared using gamma radiolysis of aqueous solutions of the polymers to effect crosslinking of the polymer chains. The molecular weight of the PVA was in the range 75–105 kDa and of PVP was 360 kDa. Gel doses were measured for the polymers and found to be 11 kGy for PVA, 3.7 kGy for PVP and 4.6 kGy for a mixture of PVA and PVP with a mole fraction of PVP of 0.19. The initial water content of the gels was 87.2 wt%. Further water uptake studies were undertaken using both gravimetric and NMR imaging analyses. These studies showed that the uptake processes followed Fickian kinetics with diffusion coefficients ranging from 1.8×10^{-11} for the PVA hydrogel to 4.4×10^{-11} $m^2\,s^{-1}$ for the PVP hydrogel for radiation doses of 25 kGy and a temperature of 310 K. At 298 K the gravimetric study yielded a diffusion coefficient of 1.5×10^{-11} $m^2\,s^{-1}$ whereas the NMR analysis yielded a slightly higher value of 2.0×10^{-11} $m^2\,s^{-1}$ for the hydrogel with a mole fraction of PVP of 0.19 and a radiation dose of 25 kGy.

1. Introduction

Both natural and synthetic polymers play key roles in modern dentistry and medicine, since polymers are essential components of a wide variety of contemporary biomaterials—from implants to contact lenses and pharmaceuticals to wound dressings. In most of these applications the biocompatibility of the polymer is an important consideration, because many polymers can evoke an inflammatory response when they come into contact with body tissues. Therefore the choice of the polymer to be used in the manufacture of any biomedical device must be tuned for the application of the material. The applications of biomedical hydrogels and the use of high-energy radiation in their formation have been reviewed (Rosiak et al., 2002).

One of the first synthetic polymers to become widely utilized in medicine was poly(methyl methacrylate), PMMA, as it was found to be relatively benign when in contact with some body tissues, for example, eye tissues. Thus PMMA became widely accepted as a safe polymer for use in dentistry and medicine, in such diverse applications as dental restoratives and contact lenses, for example. However, PMMA is a hard, inflexible material, whereas for many applications much softer materials are preferable, e.g. for breast implants. Thus soft aqueous gels of poly(hydroxyethyl methacrylate), PHEMA, were introduced in the 1950–1960s by Wichterle and Lim (1960) and used, for example, in contact lenses, and PHEMA based polymers have now become the synthetic polymer of choice for many biomedical applications.

Another synthetic polymer long utilized in medicine in the form of a hydrogel is poly(vinyl alcohol), PVA. Initially, PVA was crosslinked with formaldehyde to form a network gel, but these gels were found to degrade at the sterilization temperatures required in an autoclave. Thus a later development was to crosslink the PVA though exposure to high-energy irradiation, which also simultaneously sterilized the material (Hoffman, 1981). The body tissue response to PVA gels has been found to be mild, but they are known to undergo calcification over time when in contact with body fluids and they do not have optimum mechanical properties. Another water-soluble, synthetic polymer that evokes only a mild body response is poly (vinyl pyrrolidone), PVP. However, PVP forms a hydrogel with relatively poor mechanical strength. But it has become widely used as a comonomer in the preparation of medical hydrogels (Rosiak, 1991).

Hossen et al. (2008), have studied PVA–PVP hydrogels and have used high-energy radiation in their preparation. In particular these workers reported the effects of dose on the swelling behaviour and gel strength. They observed that the gel fraction increased with radiation dose but the swelling ratio decreased at

* Corresponding author.
E-mail address: d.hill@uq.edu.au (D.J.T. Hill).

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room temperature. Other workers have examined the use of PVA–PVP gels as biomedical materials for cartilage repair (Katta et al., 2007; Spiller et al., 2008) and the replacement of the nucleus pulposus of intervertebral discs (Thomas et al., 2003). In these studies the principal focus has been on elucidating the mechanical properties and long term stabilities of the hydrogels. Other workers (e.g. Jabbari and Karbasi, 2004; Fussell et al., 2005; Liu et al., 2009) have examined features of the PVA–PVP hydrogels when swollen in solutions which mimic body fluids, so examining the effects of occluded ions and proteins on the hydrogel properties.

To improve some of the biomedical properties of PVA hydrogels, Razzak et al. (1999, 2001, 2002) studied the preparation, properties and applications of hydrogels based upon crosslinked network gels of PVA and PVP. In particular they have examined the use of these gels as wound dressings. The PVA and PVP polymer chains in the gels were crosslinked and sterilized using high-energy radiation. These gels were reported to have advantages over both the PVA and PVP homopolymer gels for use as wound dressings, and, in particular, the gels displayed relatively high water contents, moderate water vapour transmission rates and acceptable adhesive strengths.

In their studies, Razzak and coworkers examined a range of polymer compositions and radiation doses to identify the optimal conditions for formation of the gels for wound dressings. Aqueous solutions of PVA and PVP containing ≈ 85 wt% water and a mole fraction of PVP of 0.19 irradiated to 25 kGy were found to yield gels that have optimal bioadhesion and good mechanical properties, they were soft and robust and they evoked no significant body tissue response. They identified that an important feature of these hydrogel dressings was that they were capable of absorbing more water when in use, for example from wound exudates. In addition, therapeutic drugs could be incorporated into the dressing and, when they are applied, the drugs can be released slowly from the dressing into the wound environment.

We have extended these earlier studies of Razzak and coworkers. We have studied the physical characteristics of the water uptake processes in the PVA–PVP gels, the states of the sorbed water and the calcification processes which can take place when they are in contact with body tissue (Zainuddin et al., 2001, 2002, 2004, 2007). In this paper we review our previous studies with a focus on identifying the nature of the water uptake process, and we also report some new data for these hydrogels.

2. Experimental

2.1. Materials

PVA powder with a degree of saponification of 98 mol% was obtained from Kuraray Poval Co. Ltd., Japan, as PVA-117. It had a molecular weight in the range 74.8–105.6 kDa. PVP powder was purchased from Fluka AG, Switzerland as PVP K-90 and had an average molecular weight of 360 kDa. The molecular weights of the polymers were provided by the suppliers and they were not recharacterized. Both polymers were used as received.

2.2. Preparation of hydrogels

Two solutions of 12.8 wt% polymer, one of PVA and one of PVP, were prepared by dissolving the polymer in distilled water at 100 °C. Solutions with various proportions of PVA/PVP covering the range of polymer compositions and containing 12.8 wt% polymer were also prepared using a similar procedure. After the solutions were homogenous, they were allowed to cool to room temperature and then poured into cylindrical glass moulds with a diameter of 0.3 or 0.5 cm and depth of ≈ 2.5 cm. The moulds were then covered with linear low-density polyethylene (LLDPE) film and the solutions were irradiated at room temperature in a Gamma cell facility using ^{60}Co γ-rays at a dose rate of 6.2 kGy/h to doses ranging from 0 to 60 kGy to form transparent, crosslinked hydrogels.

2.3. Sorption experiments

Cylindrical samples of gel of ≈ 0.3 cm diameter and ≈ 2.5 cm in length were cut squarely at the two ends to yield samples with a final length of ≈ 2 cm. All water sorption experiments were carried out on these samples by placing them in distilled water at controlled temperatures of 298, 310, 318 and 333 K. The samples were removed at time intervals and the excess water was removed by drying them with tissue paper. The masses were then measured on a Mettler AC 100 analytical balance. The mass uptake measurements were continued until the masses of the samples remained constant, which required approximately 2–3 weeks.

2.4. Magnetization-prepared NMR microscopy

For these studies a cylinder of diameter 0.5 cm was used with an original water content of 87.2 wt% and a PVP mole fraction of 0.19. The crosslinking dose was 25 kGy and the water sorption experiments were performed at 298 K.

The magnetization-prepared NMR microscopy experiments were performed on a Bruker AMX-300 spectrometer. The duration of the magnetization-preparation Hahn echo pulses were 14, 28 and 14 ms, and the echo times, TE*, were varied from 20 to 400 ms. The echo time in the imaging sequence was 7 ms and the recovery time was 2.0 s. The read gradient strength was 39.14 mT m^{-1} and the image was acquired over 256×256 pixels. The field of view of the images was 3×3 cm^2, and the slice thickness was 1 cm. Each image was averaged over two acquisitions, giving a total imaging time of 60 min.

3. Results and discussion

Solutions of PVA, PVP and PVA–PVP all containing 12.8 wt% polymer were prepared. Samples of these solutions were then exposed to a range of radiation doses between 0 and 60 kGy to form crosslinked hydrogels. The soluble fraction of polymer in each of the samples was then removed by hot water extraction in a Soxhlet apparatus. The extraction process was continued until the remaining gels reached a constant weight and the polymer gel and soluble fractions were then calculated using the following relationship:

$$\text{Gel fraction} = W_f/W_0 = 1-s \quad (1)$$

where W_0 and W_f are the weights of polymer in the hydrogel before and after extraction, respectively, and s is the soluble fraction of polymer.

The results for PVA, PVP and a PVP–PVP mixture with a mole fraction of PVP of 0.19 are presented in Fig. 1 in the form of a Charlesby–Pinner plot (Charlesby and Pinner, 1958) that can be expressed as

$$s+s^{0.5} = \frac{G(S)}{2G(X)} + \frac{9.6\times 10^6}{M_W G(X) D} \quad (2)$$

where $G(S)$ is the yield of chain scission, $G(X)$ is the yield of crosslinking, M_W is the molecular weight of the polymer prior to crosslinking and D is the dose in kGy. (Eq. (2) applies for radiation