The effect of THPS concentration on nPAG microstructure

C J Watson¹, J R Supple¹, A U Yeo¹², M Geso³ and R D Franich¹
¹School of Science, RMIT University, Melbourne, VIC 3001, Australia
²Physics Department, Radiation Oncology Victoria, GenesisCare, East Melbourne, VIC 3002, Australia
³School of Health and Biomedical Sciences, RMIT University, Bundoora, VIC 3083, Australia
E-mail: callum.watson@rmit.edu.au

Abstract. The microstructures formed within a normoxic polyacrylamide gel (nPAG) dosimeter and their correlation to amount of dose received is investigated through the use of two scanning electron microscope modalities. The effect of gold sputtering onto the samples was examined to determine if it impacted the detectable structures. The evolution of polymer structure with increasing dose is shown to progress from long shard like polymer chains to smooth polymer structures coating the gel surface. It is demonstrated that without gold coating the samples, which is a necessity in high vacuum scanning electron microscopy, that an environmental scanning electron microscope can be used for analysis of polymerized structures. The addition of THPS as an antioxidant is shown to not alter the formation of polymer microstructures when compared to other studies involving THPC. It is also proposed that knowledge of these features could be used to manipulate the deformability, stability and polymerized opacity of an nPAG dosimeter.

1. Introduction

The polymerized microstructure of normoxic polyacrylamide gel (nPAG) must be well understood to have certainty in a measured dose from a dosimeter. The pre and post irradiation stability, in both chemical and physical terms, can have significant effects on dose response and sensitivity [1, 2]. The molecular structure of the dosimeter volume is quite significant when quantifying these effects and could be exploited to alter and improve the dosimeter utility [3], specifically with the intent of tracking and verifying dose deformation [4].

The introduction of antioxidants such as Bis [tetrakis (hydroxymethyl) phosphonium] sulphate solution (THPS) and Tetrakis (hydroxymethyl) phosphonium chloride solution (THPC) has made it easier to fabricate dosimeters that are less susceptible to negative effects due to atmospheric oxygen interference [5-8]. With more rigorous investigation of the molecular structure of the polymer gel using techniques such as scanning electron microscopy (SEM), the physico-chemical effects of individual chemicals can be better understood and manipulated to alter or tune the dose sensitivity, temporal stability and reproducibility of nPAG dosimeters [9]. The difference between the resulting microstructures from polymerization of polyacrylamide gels containing THPS and THPC could be quantified, and SEM analysis may yield quantitative metrics for the measurement of dose response and sensitivity [10], and a means of manipulating physical properties of dosimeters or adding imaging features for tracking dose warping or measuring dose deformation [11]. The separation of gelatin...
structures in the hydrogel relative to the size of Bis and AAm is quite large [12], and it has very little influence over the diffusion rate and distance of these small molecules [13].

The effect that THPS has on polymer chain separation and resultant pore size is of interest for expanding nPAG dosimeter applications. The molecular structure variances caused by THPS when compared to THPC using environmental and high vacuum SEM have been investigated, while also describing the effect that SEM sample preparation has on polymer gel samples, namely any structural damage caused during deposition of a gold coating.

2. Materials and methods
The hydrogel examined in this study was similar that used by Yeo et al [14], where 2 wt.% gelatin was used as Sedaghat et al [9] had indicated that a gel concentration of 5 wt.% made it difficult to image fine molecular structure (<30µm). Six samples were prepared and stored in 15 ml glass vials, in which they were irradiated using a Clinac iX model. The samples were delivered maximum doses of 0, 4, 8, 12, 16 and 20 Gy from a 10x10 cm² field at 10MV while submerged in a water bath.

The samples were allowed to polymerize for 48 hours before being placed into a freezer at -80°C for 24 hours. After this period the samples were moved to an OPERON freeze dryer for 24 hours which operated at -60°C and a pressure of 0.007 mtorr. The samples were sliced thinly and mounted on a standard SEM imaging stub. A 25 nm gold layer was sputter coated onto 0, 8 and 20 Gy samples. The hydrogels were then imaged using a FEI Quanta200 SEM, the uncoated samples in low vacuum, and the gold coated samples in high vacuum modes.

3. Results and discussion
The images in Figure 1 are representative of the general structures present in each of the samples imaged in low magnification (80x). It can be seen most primarily in the 8 Gy sample (pane c) that there is large variation in the polymer chain separation across the imaged surface, indicating inhomogeneities present during the fabrication process, arising during polymerization and possible damage to the gel structure during the freeze drying process. The variance in polymer chain density is visible in Figure 1, and further magnified in Figure 2, is consistent with results determined using Raman spectroscopy [15], and the size of these structures also increases in size and length with dose until 16 Gy where the polymerization has progressed to a point that the monomer cross linking structure is no longer distinct, instead a rough surface coats much of the gelatin structure.

The surface features present after receiving radiation doses above 12 Gy are difficult to view through SEM in low vacuum conditions, and so applying a gold coating of approximately 25 nm in thickness to the gel sample allows for much higher resolution investigation of the surface topography created by polymerization. The risk in engaging a gold coating process, and indeed freeze drying, is that some of the gel and polymer structures can possibly be damaged or altered. Figure 3 evinces the large increase in resolution and sharpness of the captured images availed by the gold coating, several of the polymer structures are much more well defined even at low magnifications. The cross-linked polymer chains appear to be stable enough to sustain the gold coating without altering conformation. The images of the gold coated samples are of a quality that could be useful for image texture analysis to quantify dose, however the need to find a uniform region of depth and polymerization degree within samples makes the accuracy of dose measurements highly subject to user discretion in image capture.

4. Conclusion
This investigation describes the preparation and imaging via SEM of gold coated and uncoated nPAG samples. The images of polymer structures present in nPAG material is much sharper when gold coated and imaged on the SEM’s used in this study, and does not appear to result in any damage to the polymerized structures present in the sample. The addition of THPS has no visual influence on the formation of polymer structures within the nPAG while it does influence the size of the gel pores in the sample.
Figure 1. Low magnification SEM images of nPAG structures that have received 0 Gy(a), 4 Gy(b), 8 Gy(c), 12 Gy(d), 16 Gy(e) and 20 Gy(f). Captured on a FEI Quanta200 SEM in low vacuum mode, accelerating voltage of 15kV.

Figure 2. Environmental SEM images of nPAG samples that have received 0 Gy(a), 8 Gy(b) and 16 Gy(c) radiation doses. The samples are subject to small amounts of charge being deposited by the electron beam, resulting in saturation of some image areas.

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Images (a) and (c) are gold coated samples that have received 0 and 8 Gy respectively, with predominant feature sizes of approximately 20.0 µm, compared to images (b) and (d) which have not been gold coated and possess identical structures but are imaged in the 50.0 µm region. Image (e) is a gold coated sample that has received 20 Gy, the sample stage was tilted slightly to provide extra resolution in the depth changes present on the sample surface, the visible features in this image are less than 2 µm in size. (f) is an uncoated sample at twice the image size of (e), some of the same surface topography is visible but any higher magnification viewing of the sample resulted in charging which created artefacts that limited sharpness and the ability to capture an image displaying features that can be directly related to dose.

6. References

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