

A Study of Normoxic Polymer Gel Dosimeter Using Raman Spectroscopy Analysis

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Abstract. Radiation induced chemical changes in polyhydroxymethylacrylate gels (PHEMAG) used in 3D radiation dosimetry have been studied using Raman spectroscopy. The gels were irradiated to low energy x-ray and the polymerization of PHEMAG gels are followed by the change of Raman shift intensity of the carbon covalent bond of PHEMAG originated from both monomer and the cross-linker. The variation in peak intensities with absorbed dose was observed. The peak intensities of covalent bond of carbon in the polymer gels decrease with increasing tube voltage. This indicates that polymerization increase with higher dose of radiation. The concentration of monomers was also varied. Results show that the sensitivity of polymer gel dosimeter increases as the monomer concentration increases.

Keywords: normoxic polymer gel, Raman Spectroscopy.

1. Introduction

Current progress of complex radiotherapy treatment has point out the need of a dosimetry system that is able to measure absorbed dose distributions in three dimensional with high spatial resolution. Current dosimeters, such as ionization chamber, radiographic films and thermo luminescent dosimeter (TLD) can only measure in one or two dimension, and therefore are inadequate to integrate dose over three dimensional volumes. Hence, polymer gel dosimeter has been introduced to overcome this problem. This tissue equivalent dosimeter can measure absorbed dose distributions in three dimensions and it also allows simulation of the patient's procedures without any limitations. Popularization of polymer gel dosimeter started with the study made by [1], where polymer gel dosimetry has been used to measure absorbed dose distributions.

To date, polymer gel dosimeter are made from one or more acrylic monomers that are distributed homogeneously in a water-based gelatin matrix. Upon irradiation with ionizing radiation, polymerization happens. The polymerization of polymer gel basically initiated by free radicals generated mainly from the radiolysis of water. Hence, the presence of atmospheric oxygen is strictly prohibited as the oxygen rapidly quenched the free radicals. This problem raises a significant drawback to polymer gel dosimeter. The processes of manufacturing polymer gels are often laborious and polymer gels are sensitive to any oxygen contamination which inhibits the radiation induced polymerization. As a result, these gels have to manufactured, stored and used under hypoxic conditions.

A new formulation of polymer gel, which can be made under normal atmospheric conditions, has been introduced [2]. Because manufacturing and processing can be performed under normal atmospheric conditions, this gel is also called normoxic [3]. An anti-oxidant has been introduced into the gel to bind the atmospheric oxygen in the gel aqueous. When polymerization occurs, a number of gel properties will be altered (e.g., the NMR relaxation rates of water protons in the gel and the way the gel attenuates and scatters ultrasound and light). Thus, the response to absorbed dose can be evaluated using MRI [5], optical tomography [6], x-ray computed tomography (x-ray CT) [7], ultrasound [8] or FT-Raman spectroscopy [9,

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10, 11]. Studies concerned with understanding of basic radiation induced gel parameters have been performed using Raman spectroscopy with a vision that a better understanding of these phenomena will promote the development of improved gel dosimeters.

In this study, PHEMAG gel is used where 2-hydroxymethylacrylate as the monomer and *N, N'* –methylene-bis-acrylamide as the cross-linker. The aim of this study, which is work in progress, was to produce several batches of PHEMAG gels with different monomers concentration and to characterize the radiation induced changes in the polymer gel dosimeter produced. The monomer consumption as a function of absorbed dose was studied using Raman spectroscopy. The results are then compared among the batches of polymer gel.

Table 1. Components of the different gel batches

Batch	Component					
	<i>Gelatin (%)</i>	<i>HEA (%)</i>	<i>HEMA (%)</i>	<i>BIS (%)</i>	<i>AA (mM)</i>	<i>Water (%)</i>
PHEMAG I	8	-	2	3	35	87
PHEMAG II	8	-	3	3	35	86
PHEMAG III	8	-	4	3	35	85

2. Materials and Methods

2.1. Gel Manufacture

Polymer gel dosimeters were manufactured under normal atmospheric conditions (1.01326 bar, 60% humidity) without the use of a glove box according to [2] and [3]. The chemical components used in this experiment are gelatin (bovine skin, Type B, Sigma Chemical Co), 2-hydroxyethylacrylate (HEA) (97%, ACROS Organics), *N, N'* –methylene-bis-acrylamide (BIS) (Sigma Chemical Co), ascorbic acid (AA) (Hamburg Chemical) and deionized water. Three batches of gel were made, in which the concentration of monomer used were varied. Concentrations of chemical components used in each batch are listed in Table 1. The gelatin was given to 40% of the total amount of deionized water and allowed to swell for half an hour at room temperature (21 ± 0.5 °C). Then the gelatin solution was stirred and heated to 55°C using a magnetic stirrer/hot plate unit until a clear solution is obtained. The BIS solution and the ascorbic acid solution were prepared in separate beakers of 50% and 10% of the total amount of water. The total amount of compositions should be 100% during the preparation in order to control the parameter used. Although the amount of deionized water is varied, it will not affect the polymerization processes and data measurement. The gelatin solution was cooled down to about 35°C. BIS solution was added to the gelatin solution. Subsequently, the monomer was added into the solution and a homogeneous mixture was achieved by continuous stirring. Finally, the ascorbic acid solution was added in order to minimize the amount of additional oxygen infiltrating the gel during the time when the anti-oxidant is active. The solution was finally poured into 4 ml spectro cuvette tubes (diameter 1mm, height 4mm) and sealed with parafilm tape in order to minimize oxygen contamination through the cap of the tube. The gels were placed in a refrigerator at low temperature to solidify. Once set, gels were removed from refrigerator and allowed to equilibrate to room temperature.

2.2. Gel Irradiation

Gels were irradiated ~12h post-manufactured. All irradiations were performed on a Toshiba KX-50 X-ray Machine using 100 cm source to surface distance (SSD) set-up and 15 x 15 cm² field size. Stack of Perspex slabs (30 cm length, 30 cm width, and 1 cm height) were used as the phantom. Sufficient Perspex slabs were placed around the dosimeter to produce full scatter conditions. One tube in each batch was left unirradiated, as a control sample and the remaining sample were irradiated to tube voltages between 40 and 140 kVp and constant tube current of 10 mAs at depth of maximum dose.

2.3. Raman Spectroscopy of PHEMAG

Raman spectra for PHEMAG were undertaken after the irradiation of the gels were performed. All Raman spectra were acquired on a Horiba Jobin Yvon LabRAM HR 800 Raman Spectrometer with 514.5nm Ar⁺ laser as the excitation source.

3. Results and Discussions

Raman spectroscopy was used to monitor the monomer and cross linker consumption after the polymerization of the polymer gel. Raman spectroscopy involves inelastic light scattering process. The sample absorbed the difference in energy between the incident and scattered radiation in the form of molecular vibrations. Each molecule has a characteristic set of vibrational and/or bending modes of covalent bonds it posses. By measuring the intensity of scattered as a function of difference in wavelength between incident and scattered radiation, a chart of molecular constituents within a sample can be done. In this study, the polymer gel dosimeters have been investigated by monitoring the consumption of monomer HEA and cross linker BIS.

A Raman spectrum of an unirradiated PHEMAG is shown in figure 1. The vibrational band assignments are discussed in section 3.1. As the PHEMAG are irradiated, the intensity of the monomer and cross-linker peaks decreases.

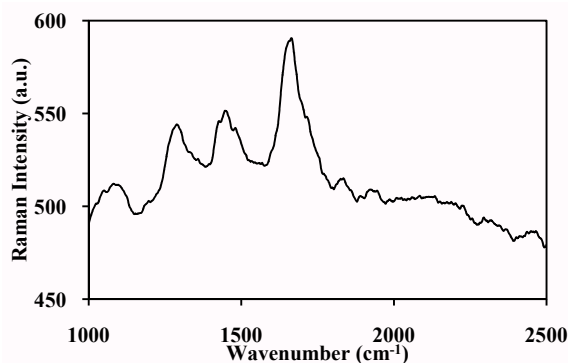


Figure 1. Raman spectrum of unirradiated PHEMAG

3.1. Vibrational band assignment

Raman frequencies of PHEMAG were characterized by referring the table of characteristics frequencies of functional groups in the Raman spectra of complex molecules from [12] and literature reports [9, 10, 11]. For all PHEAG and PHEMAG batches, spectra corresponding to each absorbed dose were plotted. For clarity, only a few representative spectra are shown (figure 2).

This study is primarily concerned with the polymerization happens after irradiation in PHEAG and PHEMAG. The polymerization process can be characterized by monitoring the consumption of monomer 2-hydroxyethylacrylate in PHEAG and 2-hydroxymethylacrylate in PHEMAG and cross-linker *N, N'* – methylene-bis-acrylamide in both PHEAG and PHEMAG during polymerization process. The consumption of the monomers and cross-linker can be monitored by observing the carbon covalent bond stretching in the polymer. The peaks chosen were at wave number 1635 cm⁻¹ and 1640 cm⁻¹ assigned to carbon covalent bond (C=C) stretching mode of PHEAG and PHEMAG respectively.

These two peaks are chosen as the primary signatures of the monomers as the peaks are well defined, relatively intense and not covered by other peaks in the same region. The exact positions of the two peaks were slightly altered between the batches (± 1 wavenumber). This can be explained by the fact that an increase in the concentration of a specific molecule will lead to increase intensity in corresponding vibrational bands-if there is an overlap with an adjacent band, the position of the corresponding peak might be slightly shifted [10].

3.2. Consumption of monomers and bis cross-linker

In general, as the polymer gel dosimeter is irradiated, monomer and cross linker are consumed (see fig. 6 of [10]). Figure 3 shows the Raman spectra for the C=C peak of PHEMAG gels. The spectra are in the range

of 1500 cm^{-1} to 1800 cm^{-1} . Observation of figure exhibit the decrease in peak intensity for the assigned peak as the tube voltage is increased. This phenomenon indicates the amount of C=C bonds for HEA decreased with increasing tube voltage. This is due to the breaking of carbon covalent bonds to single bonds and the stretching of methyl group during polymerization and cross linking of PHEMAG gel.

Figure 4 shows the Raman spectra for the C=C peak of PHEMAG gels with different concentrations irradiated with the same tube voltage. The spectra are in the range of 1550 cm^{-1} to 1750 cm^{-1} . Observation of figure exhibit the decrease in peak intensity for the assigned peak as the tube voltage is increased. This phenomenon indicates that the rate of polymerization increases as the concentration of monomer increases. This also indicates tha by increasing the concentration of monomer (2-hydroxymethylacrylate) the sensitivity of PHEMAG increase.

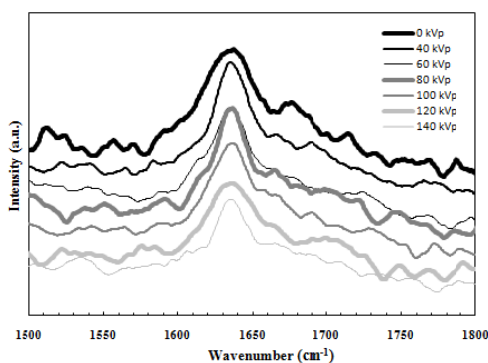


Figure 3. Raman spectra for the C=C peak of PHEMAG gels at 1640 cm^{-1} .

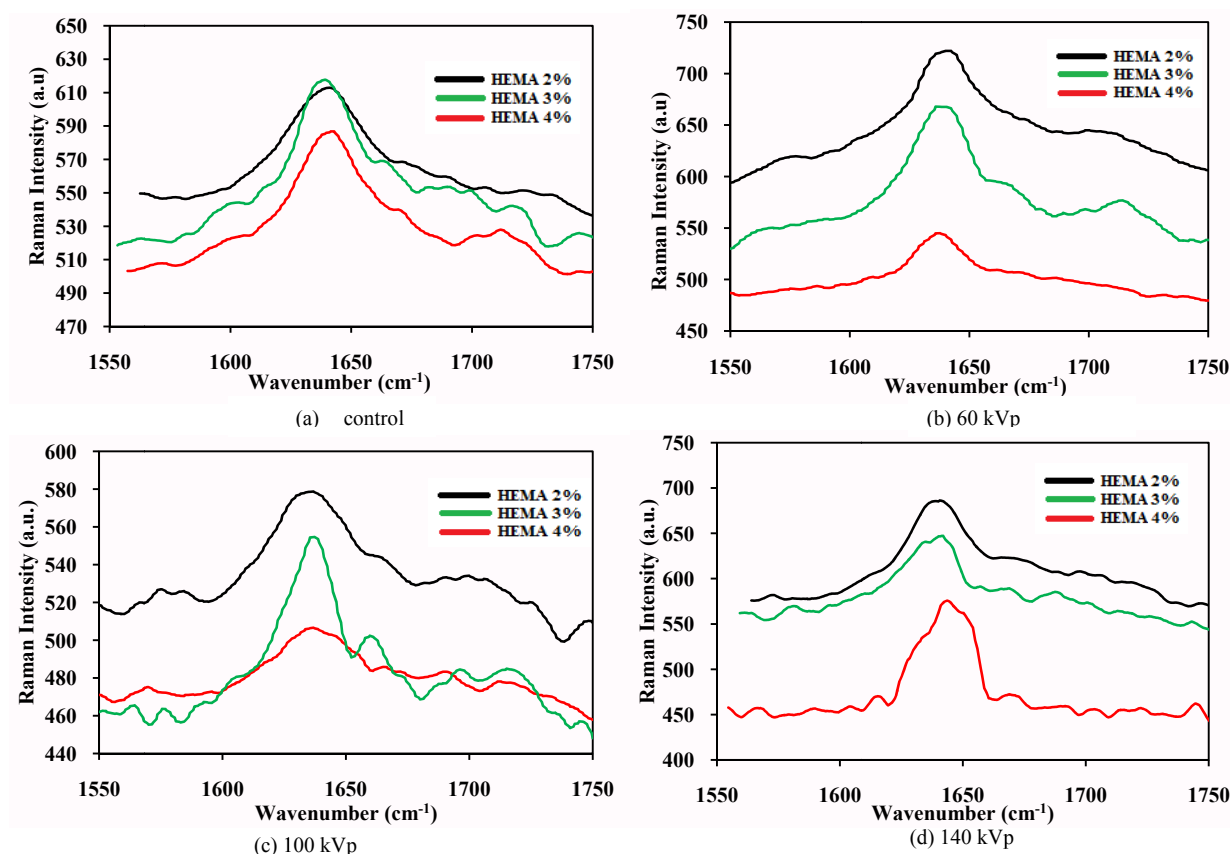


Figure 4. Raman spectra for the C=C peak of PHEMAG gels with different concentrations irradiated with the same tube voltage

4. Conclusions

Polymer gels with varying monomer concentrations manufactured using 2-hydroxymethylacrylate and BIS, were evaluated using Raman spectroscopy. The variations in peak intensities with absorbed dose were

observed. The peak intensities of covalent bond of carbon in the polymer gels decrease with increasing tube voltage. This indicates that polymerization increase with higher dose of radiation. The concentration of monomers was also varied. Results show that the sensitivity of polymer gel dosimeter increases as the monomer concentration increases. This study describes a method that can be used to characterize the polymerization of polymer gels. Future studies include variation in BIS cross-linkers which may have the advantage of more sensitivity for polymerization can be done to optimize the use of PHEMAG gels.

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6. References

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